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*A Quarterly of Research*



## CONTENTS

34599



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Abstracts of doctoral theses

1

Studies on oxygen-carrying cobalt compounds:

VIII. Analogues of disalicylalethylenediamine cobalt with o-hydroxycarbonyl compounds other than salicylaldehyde

HARVEY DIEHL, LAWRENCE M. LIGGETT, GEORGE C. HARRISON, CLIFFORD C. HACH, AND ROSS CURTIS

91

IX. Analogues of disalicylalethylenediamine cobalt with diamines other than ethylenediamine

HARVEY DIEHL, LAWRENCE M. LIGGETT, CLIFFORD C. HACH, GEORGE C. HARRISON, LOIS HENSELMEIER, R. W. SCHWANDT, AND JOHN MATHEWS, JR.

110

X. Cobalt derivatives of the Schiff's bases of salicylaldehyde with alkylamines

HARVEY DIEHL AND TSAI S. CHAO

126

34599

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# ABSTRACTS OF DOCTORAL THESES<sup>1</sup>

## CONTENTS

Some investigations of the influence of moisture content and temperature on the biological decomposition of mature plant materials	WILLIAM VICTOR BARTHOLOMEW	3
Some nitrogen and sulfur containing compounds as chemotherapeutic agents	H. SMITH BROADBENT	5
Utilization of nitrogen by the animal organism. I. When methionine serves as the main source of nitrogen in the diet of the rat	MIRIAM BRUSH	8
Some derivatives of $\gamma$ -valerolactone	ROBERT V. CHRISTIAN, JR.	11
The introduction of functional groups into some organosilanes	RUSSELL N. CLARK	15
The reaction of iodine with starch and the Schardinger dextrans	HARVEY ALBERT DUBE	19
The quantitative spectrographic analysis of the rare earth elements	VELMER ARTHUR FASSEL	21
The effect of crop rotation on soil aggregation and related characteristics in a Belinda silt loam soil	CHAO LIN FENG	24
Some substituted alkylamino sulfides and sulfones	LAWRENCE FULLHART, JR.	27
Mechanisms of addition of organolithium compounds to quinoline and isoquinoline	GORDON C. GAINER	29
Field investigation of calcium arsenate, lead arsenate, and spreading agents for codling moth sprays, and an abridged form of chi-square	LEWIS TEXADA GRAHAM	33
Ecological factors affecting the activity of the western fox squirrel, <i>Sciurus niger rufiventer</i> (Geoffroy)	ELLIS A. HICKS	36
Biology and control of the tuber flea beetle, <i>Epitrix tuberis</i> Gentner, in Nebraska	ROSCOE EARLE HILL	39
Water content changes of poultry held in frozen storage as related to palatability	HELEN VIRGINIA JOHNSON	42
The graduated land tax	RANDALL T. KLEMME	44
Evaluation of certain insecticides and drugs as chemotherapeutic agents for external blood sucking parasites	EDWARD F. KNIPLING	47
Cause and possible prevention of the cracking of thin concrete walls poured integrally with arch-ribs and rigid frames	DAVID MUIR MACALPINE	50
Linear and cyclic amylooligosaccharides and their relationship to the amylolytic enzymes	MELVIN LEWIS LEVINE	53
The mordanting of cellulose-acetate rayon, nylon, and silk with potassium dichromate	LORRAINE ANNE MERO	55

<sup>1</sup> Complete copies of these theses may be consulted at the Library, Iowa State College, Ames, Iowa.

Amylose complexes with organic acids and alkyl halides	FELIX F. MIKUS	58
The nitrogen factor in sweet potato production in Iowa	PHILIP A. MINGES	61
The manufacture of blue cheese from pasteurized milk	CARLTON EDWIN PARMELEE	64
The lipolytic enzyme system of <i>Mycotorula lipolytica</i>	ISAAC I. PETERS	66
Evaluation of amylolytic agents employed in the alcoholic fermentation	HAMIT DARWIN REESE	68
The life history and management of the white bass, <i>Lepibema chrysops</i> (Rafinesque), in Spirit Lake, Iowa	WILLIAM FRANKLIN SIGLER	71
Some factors affecting the functional properties of liquid egg albumen	HARRY MARSHALL SLOSBERG	74
The synthesis, resolution, and metabolism of tyrosine isomers and analogues	MERRILL E. SPEETER	76
Some substituted 3-indoleacetic acids	FRANK J. STEVENS	79
The generalized Laplace transformation with applications to problems involving finite differences	WILLIAM MATTHEWSON STONE	81
The effect of nitrogen fertilization on the nitrogen nutrition of legumes	GEORGE DANIEL THORNTON	84
A comparison of some laboratory methods for the production of antibodies	MARY JANE WARD	87

# SOME INVESTIGATIONS OF THE INFLUENCE OF MOISTURE CONTENT AND TEMPERATURE ON THE BIOLOGICAL DECOMPOSITION OF MATURE PLANT MATERIALS<sup>1</sup>

WILLIAM VICTOR BARTHOLOMEW

*From the Department of Agronomy, Iowa State College*

Water sorption of mature plant materials from moist atmospheres and the influence of resulting moisture contents on the initiation and rate of microbial decomposition were determined. From a moisture saturated atmosphere, water sorption was found to range from 30 to 65 per cent, according to the kind of plant material. From unsaturated atmospheres, the water sorption was proportionately less and was determined by the relative humidity and temperature as well as by the previous treatment of the sorbent. Plant materials were found to absorb moisture more rapidly at high than at low temperatures. Moisture content at equilibrium, however, was greater at low than at high temperatures. It was observed that the general features of the relative humidity-moisture content relationship of the plant materials could be expressed by the

mathematical equation  $y = \frac{ax}{1-x} + c$  where  $y$  = the moisture per cent,

$x$  = the relative humidity and  $a$  and  $c$  are constants characteristic of a particular plant material.

In both the saturated and the unsaturated range the moisture content of the plant material had a pronounced influence upon the rate of microbiological decomposition. At high moisture contents decomposition proceeded rapidly, but at very low moisture contents active biological decomposition was found to be inhibited. The threshold moisture conditions for active microbiological growth varied among the several plant materials under study and are indicated as follows: for alfalfa, 20 per cent moisture and 75-80 per cent relative humidity; for sudan grass, 14-16 per cent moisture and 77-82 per cent relative humidity; for oat straw and hemp bark, 15-17 per cent moisture and 77-82 per cent relative humidity; for pine needles, 15-17 per cent moisture and 80-86 per cent relative humidity; and for sudan grass roots, 10-12 per cent moisture and 80-86 per cent relative humidity. The moisture tensions associated with the inhibition of microbiological activity are much higher than those which cause permanent wilting of field crops. The former occurs in the relative humidity range of 75-86 per cent, whereas, the latter occurs at a relative humidity of about 98.8 per cent.

<sup>1</sup> Doctoral thesis No. 839, submitted March 20, 1947.



The moisture in the several parts of the biological range was not equally available to the microorganisms or uniformly effective in promoting their growth. In the unsaturated range moisture increases above the threshold values resulted in a rapid and proportionate increase in microbiological decomposition. In the saturated range or at moisture contents greater than those obtaining in a saturated atmosphere successive increments of moisture had a diminishing influence on decomposition.

# SOME NITROGEN AND SULFUR CONTAINING COMPOUNDS AS CHEMOTHERAPEUTIC AGENTS<sup>1</sup>

H. SMITH BROADBENT

*From the Department of Chemistry, Iowa State College*

General reviews were made of the chemotherapy of malaria, tuberculosis, and hyperthyroidism, and of the general methods recorded in the chemical literature for the preparation of diaryl sulfides and sulfones, quinoxalines, and 2-thiouracils. A series of each of these four types of compounds was synthesized for examination as possible chemotherapeutic agents.

Most of the recently developed drugs which have shown promise as antituberculous agents have been compounds containing the *p*-aminophenylsulfonyl group attached to an aromatic or heterocyclic ring.

The new thiophenol, *p*-isopropylthiophenol, b.p. 100-4.5°/14 mm., was prepared by the chlorosulfonation of cumene, followed by reduction of the sulfonyl chloride with zinc and dilute sulfuric acid. The chlorothiophenols were obtained from the corresponding chloroanilines. The following diphenylsulfides and sulfones, listed with their respective melting points (uncorr.), were prepared by condensing sodium thiophenoxides with the appropriate nitroaryl halides to form the nitro sulfides, which were oxidized to sulfones with hydrogen peroxide and which were reduced to the amines by an improved general method, which has heretofore been reported as impracticable due to catalyst poisoning, involving reduction with hydrogen over Raney nickel. The amines were converted to the pyrrol derivatives with acetylacetone.

Sulfides: 2-nitro, 80.5°; 2'-methyl-2-nitro, 87-8°; 3'-methyl-2-nitro, 86-6.5°; 4'-methyl-2-nitro, 89-90°; 4-nitro, 55°; 2'-methyl-4-nitro, 64-5°; 3'-methyl-4-nitro, 47°; 4'-methyl-4-nitro, 80-1°; 2'-chloro-4-nitro, 113-4°; 3'-chloro-4-nitro, 71-1.5°; 4'-chloro-4-nitro, 83-4°; 4'-isopropyl-4-nitro, 47.5-8.5°; 3'-methyl-2,4-dinitro, 99.5-100.5°; 3'-chloro-2,4-dinitro, 108-9°; 4'-chloro-2,4-dinitro, 121-2°; 4'-isopropyl-2,4-dinitro, 95.5-6.5°; 2-amino, 43°; 2'-methyl-2-amino, 89-90.5°; 3'-methyl-2-amino, b.p./1 mm. 174-7°; 4'-methyl-2-amino, 48.5-9°; 4-amino, 95°; 2'-methyl-4-amino, 51.5-2°; 3'-methyl-4-amino, 72.5-3°; 4'-methyl-4-amino, 72-3°; 2'-chloro-4-amino, 77-8°; 3'-chloro-4-amino, 72-2.5°; 4'-chloro-4-amino, 60-1°; 4'-isopropyl-4-acetylamino, 93.5-4.5° and 108-9° (double m.p.); 3'-methyl-2,4-diamino, 112-2.5°; 3'-chloro-2,4-diamino, 94-5°; 4'-chloro-2,4-diamino, 141-2°; 4'-isopropyl-2,4-diamino, 93.5-4°; 3'-methyl-4-acetylamino, 121-2°; 3'-methyl-4-formylamino, 72.5-3.5°; 3'-methyl-4-ureido, 150-1°; 2-(2,5-dimethyl-1-pyrrol), 116-7°; 2'-methyl-2-(2,5-dimethyl-1-pyrrol), 107-8°;

<sup>1</sup> Doctoral thesis No. 812, submitted August 23, 1946.

4'-methyl-2- (2,5-dimethyl-1-pyrryl), 78–85°; 4- (2,5-dimethyl-1-pyrryl), 86.5–7°; 2'-methyl-4- (2,5-dimethyl-1-pyrryl), 111.5–°2; and 3'-methyl-4- (2,5-dimethyl-1-pyrryl), 66°.

Sulfones: 4-nitro, 143°; 2'-methyl-2-nitro, 144–5°; 3'-methyl-4-nitro, 121–2°; 4'-methyl-4-nitro, 171–2°; 2'-chloro-4-nitro, 160–1°; 3'-chloro-4-nitro, 142–4°; 4'-chloro-4-nitro, 182–3°; 4'-isopropyl-4-nitro, 109–11°; 3'-methyl-2,4-dinitro, 128–9°; 3'-chloro-2,4-dinitro, 155–6°; 4'-chloro-2,4-dinitro, 168–9°; 4'-isopropyl-2,4-dinitro, 118–9°; 4-amino, 174–5°; 3'-methyl-4-amino, 184.5–5.5°; 4'-methyl-4-amino, 181–2°; 2'-chloro-4-amino, 142–4°; 3'-chloro-4-amino, 189–90°; 4'-chloro-4-amino, 184–5°; 4'-isopropyl-4-amino, 154.5–5.5°; 3'-methyl-2,4-diamino, 153–4°; 4'-chloro-2,4-diamino, 200.5–1.5°; 4- (2,5-dimethyl-1-pyrryl), 153–4°; 3'-methyl-4- (2,5-dimethyl-1-pyrryl), 121–2°; and 4'-methyl-4- (2,5-dimethyl-1-pyrryl), 148–9°.

The results of all the pharmacological tests are not yet available; however, many of these compounds showed significant tuberculocidal activity.

Basically substituted quinoxalines were investigated for possible chemotherapeutic activity because of their structural relationships to known compounds possessing high activities against either malaria or tuberculosis.

Improved techniques for preparing several of the required intermediates are given. The following quinoxalines were synthesized by condensing the appropriately substituted *o*-phenylenediamines and  $\alpha$ -dioxo compounds together: 2,3-dimethyl-6-amino, 186–7°; 6-amino-2,3-bis (*p*-methoxyphenyl), 194–6°; 6-amino-2,3-diphenyl, 172–3°; 6-amino-2,3-bis (*o*-chlorophenyl), 178–9°; 2,3-bis (*p*-nitrophenyl), 203–4°; 2,3-bis (*p*-hydroxyphenyl), 326–8°; and 6-amino-2,3-bis (*p*-hydroxyphenyl), 338–40°. 2,3-Bis (*p*-nitrophenyl) quinoxaline was reduced catalytically to 2,3-bis (*p*-aminophenyl) quinoxaline, 260–2°.

From the corresponding amines the following pyrrole derivatives were obtained: 6- (2,5-dimethyl-1-pyrryl)-2,3-dimethyl, 161–3°; 6- (2,5-dimethyl-1-pyrryl)-2,3-bis (*p*-methoxyphenyl), 189–90°; 6- (2,5-dimethyl-1-pyrryl)-2,3-diphenyl, 151–3°; and 6- (2,5-dimethyl-1-pyrryl)-2,3-bis (*o*-chlorophenyl), 211–12°. The tuberculocidal tests indicate slight to moderate activity. Information on their antimalarial activity is restricted.

The most effective antithyroid agents discovered in recent years have been derivatives of 2-thiouracil. Several new derivatives have been synthesized and are being tested for antituberculous as well as antithyroid activity.

By the alkylation of sodio acetoacetic ester, 1-diethylamino-4-carbethoxyhexanone-5, b.p. 100–7° (very largely 104–5°)/0.4 mm., and 1-( $\gamma$ -diethylaminopropylmercapto)-3-carbethoxypentanone-4, b.p. 147–50°/0.4 mm., were prepared.

No products could be isolated from the condensations of the above  $\beta$ -oxoesters with thiourea in the presence of sodium ethoxide.

By a modification of the Claisen condensation the ethyl  $\alpha$ -,  $\beta$ -, and

$\gamma$ -pyridoylacetaes were obtained in high yields. Modifications in the published methods of preparation of the precursory ethyl pyridoates also gave greatly improved yields. Carbethoxylation of the appropriate ketones with sodamide and ethyl carbonate gave ethyl *p*-anisoylacetate, b.p. 155–8°/0.6 mm. and ethyl  $\beta$ -(2-thienyl)- $\beta$ -oxopropionate, b.p. 121–3°/0.4 mm.

Condensation of these  $\beta$ -oxoesters with thiourea in the presence of sodium ethoxide yielded 6-( $\alpha$ -pyridyl)-2-thiouracil, m.p. 291–4° (dec.), 6-( $\beta$ -pyridyl)-2-thiouracil, m.p. 296–8° (dec.), 6-( $\gamma$ -pyridyl)-2-thiouracil, dec. 355–8°, 6-(*p*-methoxyphenyl)-2-thiouracil, softens 285, melts 288–99° dec.; and 6-( $\beta$ -thienyl)-2-thiouracil, dec. 293–6°.

From the corresponding substituted alkyl halides refluxed in ethanol with the monosodium salt of 6-methyl-2-thiouracil, 2-( $\gamma$ -diethylamino-propylmercapto)-4-hydroxy-6-methylpyrimidine, b.p. 183–8°/0.4 mm.; 2-(*p*-nitrobenzylmercapto)-4-hydroxy-6-methylpyrimidine, m.p. 220–1°, and 2-(*p*-nitrophenethylmercapto)-4-hydroxy-6-methylpyrimidine, m.p. 224–6° (slow dec.) were secured. The attempted preparation of the amino analogs of the two nitro derivatives by catalytic reduction gave only resinous polymers.

The results of the pharmacological tests on these compounds are not yet available.

The following miscellaneous heterocyclic derivatives were synthesized: 2-*n*-butyl-4-methylpyridine, b.p. 201–2°/740 mm., its picrate, m.p. 88.5–90.5°; 2-( $\alpha$ -thienyl)-6-methoxyquinoline, m.p. 137–8.5°; its picrate, m.p. 190.5–2°; 1-dimethylaminomethyl-2-hydroxydibenzofuran, m.p. 114–5°; and 2-(*p*-hydroxyphenyl)-6-methoxycinchoninic acid, dec. ca. 305–10°. None of these compounds was active against either malaria or tuberculosis.

# UTILIZATION OF NITROGEN BY THE ANIMAL ORGANISM

## 1. WHEN METHIONINE SERVES AS THE MAIN SOURCE OF NITROGEN IN THE DIET OF THE RAT<sup>1</sup>

MIRIAM BRUSH

*From the Department of Foods and Nutrition, Iowa State College*

Observations in the Nutrition Laboratory of the Foods and Nutrition Department indicate that the quantity of nitrogen excreted in the urine by rats maintained on a nitrogen-low diet decreases substantially following the incorporation of dried whole eggs in the ration. This depression, contraindicated by all concepts of a constant "endogenous" nitrogen metabolism, is accompanied by the sparing of body nitrogen as calculated from nitrogen balance data, and by a restoration of the body weight lost in the previous period when the ration deficient only in nitrogenous constituents was fed. The present study reports the identification of the specific components of the dried eggs which were effective in sparing body nitrogen, an evaluation of the relative capacity of each of these compounds in regard to their ability to spare body tissue, and results of further investigation into the mechanism of body-sparing action.

The nitrogen balance test was employed, albino rats being used as the test animals. Metabolism studies were made during the period when the basal nitrogen-low diet, alone, was fed, and in a subsequent period when the basal ration was supplemented with some source of nitrogen.

The effect of feeding the basal diet and of supplementing it with certain nitrogenous constituents was evaluated in terms of the quantity of urinary nitrogen excreted, the nitrogen balance in each metabolism period, and the "body nitrogen spared," i.e., the difference between the balances in the two metabolism periods. Several studies were carried out, as described below.

The feeding of a supplementary mixture of the ten essential amino acids caused a depression in the urinary excretion of nitrogen and a body-sparing effect essentially the same as that resulting from the similar administration to partially depleted rats of dehydrated eggs equivalent to 3.5 per cent of protein. The body nitrogen spared, when converted to its equivalent in body tissue, was equal to the losses in body weight prevented by supplementary feeding.

Methionine given as the sole dietary source of nitrogen to rats, following a period of feeding of the low-nitrogen diet, reduced the quantity of nitrogen excreted in the urine, and prevented a loss of body nitrogen equivalent to 5 gm. of tissue. Although the animals fed methionine failed to gain weight, they lost 5 gm. less than they would have, had no methionine been offered.

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<sup>1</sup> Doctoral thesis No. 806, submitted July 20, 1946.

In contrast to the effect of feeding the complete amino acid mixture, a mixture composed of all the essential amino acids except methionine fed to protein-depleted rats caused a marked increase in the excretion of urinary nitrogen.

When each of the ten essential amino acids was fed separately in the routine nitrogen balance test, methionine, arginine, and histidine, only, caused a depression in the urinary excretion of nitrogen reflected in a definite sparing of body tissue. In addition to these three amino acids, leucine and lysine also spared some body tissue, seemingly exerting their effect by diminishing the excretion of nitrogen via the gut. Phenylalanine appeared to stimulate the breakdown of body tissue, as indicated by an increase in the negative nitrogen balance in the period of nitrogen feeding. Some disturbance in metabolism was evident following the feeding of tryptophane, when a yellow pigment was excreted in the urine.

Egg proteins fed to groups of rats in amounts representing 1 to 4 per cent of the quantity of the nitrogen-low ration consumed during the first balance period caused nearly identical depressions in the urinary excretion of nitrogen at each level of intake. The amount of body nitrogen spared increased with each increase in the quantity of egg proteins fed. On the other hand, the magnitude of the depression in the excretion of urinary nitrogen decreased with increasing amounts of methionine in the diet, and, interestingly, the same amount of body nitrogen was spared at each level of methionine feeding.

Dietary cystine and choline ranked very close to methionine not only in regard to the relative magnitude of the depression in the quantity of nitrogen excreted in the urine, but in the quantity of body nitrogen spared.

The quantities of nitrogen and methionine in the carcasses of animals killed at specific intervals of the balance test were determined. As a result of feeding the nitrogen-low diet for 18 days, the nitrogen content of the whole carcasses of rats decreased from 8.38 gm. to 6.41 gm. The body weight declined correspondingly. Neither the administration of methionine as a supplement to the nitrogen-low diet, nor the feeding of the nitrogen-low diet alone for an additional 11 days, had any further effect on the nitrogen content of the whole carcass. However, the addition of egg proteins to the diet for 11 days brought the nitrogen content of the carcass to 7.75 gm., the increment being equivalent to the body weight regained during this period. The per cent of nitrogen in all carcasses was the same, 2.6 per cent.

The total methionine content of the carcass fell during the first 18 days of nitrogen-low feeding, but remained constant thereafter, whether the nitrogen-low diet was fed alone or with methionine. Egg proteins given during the last 11 days of the balance period caused an increase in the total methionine corresponding to the increase in total nitrogen. The per cent of methionine nitrogen to total nitrogen in the carcasses of all groups analyzed remained constant.

The livers of animals fed a nitrogen-low diet for 29 days contained

slightly less nitrogen than did those of animals whose diets were supplemented in the last 11 days of the nitrogen balance test with methionine. The ratio of methionine nitrogen to total nitrogen was the same in the livers of both groups, 3.0 per cent.

The concentration of methionine per gram of dry, fat-free muscle was constant under all conditions of dietary manipulation.

The fat content of muscle tissue was constant despite dietary changes. Hepatic tissue reflected the dietary lack of nitrogen by a rise in the concentration of fat, a condition not corrected by the feeding for 11 days of supplementary egg proteins, choline, or a mixture of the ten essential amino acids. Supplementary methionine and cystine in the ration caused a marked increase in the fat content of the liver.

Thus, it seems that the effect of the introduction of egg proteins into a ration deficient in protein on the nitrogen metabolism of the rat may be ascribed to the presence of the essential amino acids. Methionine, which is the most powerful in sparing body protein, probably acts largely through its capacity to form cystine, choline, or related compounds. No single amino acid, however, can be very important quantitatively in sparing body tissue in the partially depleted animal, in view of the complex demands of the body for the synthesis of its structural and functional components. Egg proteins and a mixture of the essential amino acids are much more effective in this respect than is any individual amino acid, as indicated by the quantities of body nitrogen spared and by restoration of weight lost when the nitrogen-poor ration was fed.

Analyses of whole carcass, liver, and muscle of adult rats suggest that the effect of methionine on nitrogen metabolism does not represent the over-all picture of nitrogen metabolism, wherein amino acids in the metabolic pool arising from food and tissue sources are used in the maintenance of body tissue and in the synthesis of functional proteins and of nitrogenous and non-nitrogenous metabolites. Continued loss in body weight, the lack of change in the total nitrogenous content of the carcass, and the relatively small increment in labile reserves in the liver when methionine is fed to the depleted animal, suggest that methionine does not act in the maintenance of body tissues. The powerful effect of dietary methionine and cystine and the somewhat less pronounced influence of arginine and histidine in decreasing the losses of nitrogen in the urine of animals maintained on a nitrogen-low diet are evidence that the body does raid its tissues for specific metabolites for the synthesis of specific functional substances.

# SOME DERIVATIVES OF $\gamma$ -VALEROLACTONE<sup>1</sup>

ROBERT V. CHRISTIAN, JR.

*From the Department of Chemistry, Iowa State College*

Some of the reactions of  $\gamma$ -valerolactone and its reduction product, 1,4-pentanediol, have been examined in anticipation that new derivatives might prove worthy of industrial applications. Attention was directed to the possibility of using  $\gamma$ -valerolactone and 1,4-pentanediol as starting points in the synthesis of bifunctional acids and amines from which linear polyamides of the "nylon" type could be prepared. One phase of the study proved to be a new approach to the synthesis of  $\beta$ -alkoxypropionic acid and necessitated an extension of the investigation to a series of structurally related compounds.

In verification of the work of Eijkman (1),  $\gamma$ -valerolactone was found to react with benzene in the presence of aluminum chloride to yield 61 per cent of  $\gamma$ -phenylvaleric acid (*p*-bromophenacyl ester, m.p. 76°). Proof that  $\gamma$ -phenylvaleric acid prepared in this way was identical with that obtained by other methods (2,3,4,5) was afforded by ring closure to 4-methyl-1-tetralone (3,5) and preparation of 4-methyl-1-tetralone semicarbazone. (2,3,5)

Attempts to condense benzene with two molecular equivalents of  $\gamma$ -valerolactone gave mixtures from which, subsequent to esterification, there was isolated diethyl  $\gamma,\gamma'$ -phenylene-divalerate of boiling point 165–169°/0.5 mm.,  $d_4^{25}$  1.0212, and  $n_D^{25}$  1.4914. This compound was not obtained as the free acid, nor was the orientation of the substituents in the benzene ring determined.

Improved yields were obtained in the re-examination of some previously reported (6,7,8) methods for the preparation of 1,4-pentanediol by catalytic hydrogenation. The reactions were carried out without solvent in the presence of copper-chromium oxide catalyst.  $\gamma$ -Valerolactone, at 300 atmospheres and 250–290°, gave 32–83 per cent of 1,4-pentanediol. Lower yields of the glycol were obtained at the higher reduction temperatures and from these preparations 2-methyltetrahydrofuran was isolated and identified. Ethyl levulinate, at 250° and 250 atmospheres' pressure, gave 72 per cent of 1,4-pentanediol. Levulinic acid, at 267 atmospheres and 245–300°, yielded 11 per cent of  $\gamma$ -valerolactone and 44 per cent of 1,4-pentanediol.

1,4-Pentanediol was treated with acrylonitrile in the presence of 40 per cent aqueous potassium hydroxide (9) to yield 83 per cent of 1,4-di-(2-cyanoethoxy)-pentane of boiling point 157°/1 mm.,  $n_D^{28}$  1.4478, and  $d_4^{28}$

<sup>1</sup> Doctoral thesis No. 809, submitted July 22, 1946.



1.005. This compound was characterized by conversion to the solid bis-(ethyliminoester hydrochloride) melting with decomposition at 103–104°.

A series of 14  $\beta$ -alkoxypropionitriles was prepared by the addition of acrylonitrile to appropriate alcohols (10) and glycols (9). Six of these compounds were prepared for the first time. The yields and physical constants were as follows:  $\beta$ -*n*-propoxypropionitrile, 83 per cent, b.p. 87–89°/24 mm. or 84°/19 mm.,  $d_4^{20}$  0.8988,  $n_D^{20}$  1.4131;  $\beta$ -*iso*-butoxypropionitrile, 81 per cent, b.p. 88–90°/19 mm. or 91°/20 mm.,  $d_4^{20}$  0.8821,  $n_D^{20}$  1.4143;  $\beta$ -*sec*-butoxypropionitrile, 79 per cent, b.p. 90°/19 mm.,  $d_4^{20}$  0.8880,  $n_D^{20}$  1.4156;  $\beta$ -*iso*-amyloxypropionitrile, 82 per cent, b.p. 99°/13 mm.,  $d_4^{20}$  0.8818,  $n_D^{20}$  1.4218;  $\beta$ -*sec*-amyloxypropionitrile, 70 per cent, b.p. 98°/16 mm.,  $d_4^{20}$  0.8844,  $n_D^{20}$  1.4205;  $\beta$ -allyloxypropionitrile, b.p. 95°/24 mm. or 92°/19 mm.,  $d_4^{20}$  0.9380,  $n_D^{20}$  1.4330.

1,4-Di-(2-cyanoethoxy)-pentane was hydrogenated at 100–120° and 130–200 atmospheres in the presence of Raney nickel and liquid ammonia to give 77–82 per cent of 1,4-di-(3-aminopropoxy)-pentane of boiling point 132–135°/2 mm.,  $d_4^{24}$  0.9448, and  $n_D^{24}$  1.4596. The diamine was miscible with water in all proportions and its 5 per cent aqueous solution exhibited a pH in excess of 11. The picrate and hydrochloride of 1,4-di-(3-aminopropoxy)-pentane were obtained as uncrystallizable oils.

From 1,4-di-(3-aminopropoxy)-pentane a series of normal and acid salts was prepared using monobasic and dibasic acids. The diacetate, dipropionate, dibutyrate, dilevulinate, dibenzoate, malonate, glutarate, itaconate, dimalonate, diglutarate, and diphthalate were obtained as uncrystallizable oils or gums. The solid salts and their melting points were as follows: disulfamate, about 65°; oxalate, 196–198°; succinate, 121–122°; adipate, 136–138°; sebacate, about 50°; maleate, 129–131°; phthalate, 125–126°; dioxalate, 108–110°; disuccinate, 92–94°; diadipate, 102–103°; and dimaleate, 80–85°. These salts were very soluble in water and, with the exception of the normal oxalate, easily soluble in absolute ethanol.

The saponification of 1,4-di-(2-cyanoethoxy)-pentane, di-(2-cyanoethyl)-ether, and  $\beta$ -ethoxypropionitrile by means of 9 per cent to 22 per cent sodium hydroxide gave complex mixtures. From the basic hydrolysis of  $\beta$ -ethoxypropionitrile there was isolated a substance which displayed some of the properties of acrylic acid. A mechanism is suggested for the decomposition of  $\beta$ -alkoxypropionitriles under conditions of basic hydrolysis.

Hydrolysis of  $\beta$ -alkoxypropionitriles with concentrated hydrochloric acid at 70–100° was found to be a fairly general method for the preparation of  $\beta$ -alkoxypropionic acids. Ten monobasic  $\beta$ -alkoxypropionic acids were prepared and characterized as *p*-bromophenacyl esters. Yields,

physical constants for hitherto unreported compounds, and data concerning the derivatives were as follows:  $\beta$ -Ethoxypropionic acid, (11) 86 per cent, (*p*-bromophenacyl ester, large leaflets, m.p. 47–48°);  $\beta$ -*n*-propoxypropionic acid, (12) 80 per cent, (*p*-bromophenacyl ester, shiny leaflets, m.p. 57–58°);  $\beta$ -*iso*-propoxypropionic acid, (12) 60 per cent, (*p*-bromophenacyl ester, platelets, m.p. 44–44.5°);  $\beta$ -*n*-butoxypropionic acid, 69 per cent, b.p. 96–97.5°/1 mm.,  $n_D^{20}$  1.4268,  $d_4^{20}$  0.9929, (*p*-bromophenacyl ester, shiny leaflets, m.p. 55°);  $\beta$ -*iso*-butoxypropionic acid, 67 per cent, b.p. 88–89°/1 mm.,  $n_D^{20}$  1.4227,  $d_4^{20}$  0.9843, (*p*-bromophenacyl ester, fibrous needles, m.p. 57.5–58.5°);  $\beta$ -*sec*-butoxypropionic acid, 56 per cent b.p. 90–91.4°/1 mm.,  $n_D^{20}$  1.4252,  $d_4^{20}$  0.9946, (*p*-bromophenacyl ester, oil);  $\beta$ -*iso*-amloxypropionic acid, (13,14) 69 per cent, (*p*-bromophenacyl ester, glistening needles, m.p. 56°);  $\beta$ -*sec*-amyloxypropionic acid, 49 per cent, b.p. 100–101.4°/1 mm.,  $n_D^{20}$  1.4289,  $d_4^{20}$  0.9833, (*p*-bromophenacyl ester, oil);  $\beta$ -allyloxypropionic acid, 33 per cent, b.p. 84°/1 mm. or 111–112°/6 mm.,  $n_D^{20}$  1.4423,  $d_4^{20}$  1.0604, (*p*-bromophenacyl ester, platelets, m.p. 38–39°);  $\beta$ -(2-methoxyethoxy)-propionic acid, 75 per cent, b.p. 110°/0.5 mm.,  $n_D^{20}$  1.4356,  $d_4^{20}$  1.1146, (*p*-bromophenacyl ester, oil, m.p. about 15°).

The same hydrolysis procedure served for the preparation of four dibasic acids of the  $\beta$ -alkoxypropionic type. These were characterized by conversion to simple amides *via* the acid chlorides which were not isolated. The acids and their derivatives were as follows: di-(2-carboxyethyl)-ether, 97 per cent, m.p. 60–61°, b.p. 189–192°/less than 1 mm., (amide, (9) m.p. 144°); 1,2-di-(2-carboxyethoxy)-ethane, 94 per cent, m.p. 66°, (amide, (15) m.p. 123°); 1,3-di-(2-carboxyethoxy)-propane, 90 per cent, m.p. 86–87°, (amide, m.p. 124°); di-(2-[2-carboxyethoxy]-ethyl)-ether, 91 per cent, undistillable, uncrystallizable oil, (amide, (15) m.p. 103–103.5°).

1,4-Di-(2-cyanoethoxy)-pentane underwent a partial cleavage during treatment with concentrated hydrochloric acid at 75–100°. From the resulting mixture there was isolated, subsequent to esterification, a chlorine-containing compound of boiling point 109–112°/2.5 mm.,  $d_4^{25}$  1.0325, and  $n_D^{25}$  1.4386. The complete analysis of this compound was in close agreement with that calculated for an ethyl  $\beta$ -(chloroamyloxy)-propionate.

1,4-Di-(2-carboethoxyethoxy)-pentane (b.p. 151–153°/1 mm.  $d_4^{25}$  1.0174,  $n_D^{25}$  1.4363) was prepared by two methods, both of which involved the hydrolysis, at room temperature, of an initially-formed mineral acid salt of the *bis*-ethyliminoester of 1,4-di-(2-cyanoethoxy)-pentane.

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# THE INTRODUCTION OF FUNCTIONAL GROUPS INTO SOME ORGANOSILANES<sup>1</sup>

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It was the primary purpose of this thesis to prepare organosilanes which contained functional groups and which so lent themselves to more fundamental studies. In particular, one of the broader purposes was to investigate the general relationships between the chemistry of similar silicon and carbon molecules.

Tetraphenylsilane was synthesized by the addition of four equivalents of phenyllithium to one of either silicon tetrachloride or tetraethoxysilane or tetrathioethoxysilane. The yields varied from 97–99 per cent; the time of reaction was only that required to complete addition of the reagents. Similarly, the following compounds were prepared: tetraethylsilane (92 per cent), b.p., 150–151°/739 mm.; tetra-*n*-butylsilane (97 per cent), b.p., 156–157°/739 mm.;  $d_4^{20}$  0.8008;  $n_D^{20}$  1.4465;  $MR_D$ , calcd. 85.49;  $MR_D$ , found 85.19.

Tetraisopropylsilane could not be prepared by this general method; treatment of silicon tetrachloride or tetraethoxysilane with four equivalents of isopropyllithium gave triisopropylchlorosilane and triisopropylethoxysilane, respectively. Their constants were: triisopropylchlorosilane, b.p., 198°/739 mm.;  $d_4^{20}$  0.9008;  $n_D^{20}$  1.4518;  $MR_D$ , calcd. 58.00;  $MR_D$ , found 57.81; triisopropylethoxysilane, b.p., 200°/738 mm.;  $d_4^{20}$  0.8657;  $n_D^{20}$  1.4560;  $MR_D$ , calcd. 63.37;  $MR_D$ , found 63.18. Triisopropylchlorosilane reacted with ethanol in the presence of pyridine to give triisopropylethoxysilane (95 per cent).

Triphenyl-*p*-tolylsilane (91 per cent), m.p. 134–135°, was synthesized by the careful addition of three equivalents of phenyllithium to one of silicon tetrachloride followed by the addition of one equivalent of *p*-tolyllithium. Similarly, these compounds were prepared: tri-*p*-tolylphenylsilane (89 per cent), m.p. 127–128°; triphenylmethylsilane (92 per cent), m.p. 66–67°; trimethylphenylsilane (89 per cent), b.p., 163–164°/737 mm.;  $n_D^{20}$  1.4890.

When trimethylphenylsilane was synthesized by the addition of one equivalent of methyllithium to one of silicon tetrachloride followed by the addition of three equivalents of phenyllithium the yield was only 23 per cent.

<sup>1</sup> Doctoral thesis No. 826, submitted December 16, 1946.

Diphenyldi-*p*-tolylsilane (78 per cent), m.p. 176–177°, was prepared by adding two equivalents of phenyllithium to one of silicon tetrachloride and then adding two equivalents of *p*-tolylolithium.

The action of three equivalents of phenyllithium upon one of silicon tetrachloride gave a reaction mixture which was hydrolyzed to give triphenylsilanol (97 per cent), m.p. 150–151°.

Triphenylethoxysilane (68 per cent), m.p. 64–65°, was synthesized by reacting three equivalents of phenyllithium with one of tetraethoxysilane. Hexaphenyldisiloxane (28 per cent), m.p. 220–221°, was also isolated from this reaction.

*p*-Bromophenyltrimethylsilane (73 per cent) was prepared by first adding one equivalent of *p*-bromophenylmagnesium bromide to one of triethoxychlorosilane and then adding three equivalents of methylolithium to this reaction mixture, b.p., 94–95°/2.5 mm.;  $d_4^{20}$  1.2023;  $n_D^{20}$  1.5272;  $MR_D$ , calcd. 57.52;  $MR_D$ , found 57.48. This compound reacted with lithium to give the corresponding organolithium compound. Carbonation of this derivative gave *p*-carboxyphenyltrimethylsilane (60 per cent), m.p. 110–111°.

Benzyltriethoxysilane (65 per cent), b.p. 245–248°/739 mm., was synthesized by the action of one equivalent of benzylmagnesium chloride upon one of triethoxychlorosilane. This same procedure was used to prepare phenyltriethoxysilane (66 per cent); b.p. 228–230°/741 mm.

Benzyltriethoxysilane, when treated with three equivalents of methylolithium, gave benzyltrimethylsilane (93 per cent), b.p., 185–187°/736 mm.

When benzyltriethoxysilane was treated with three equivalents of methylmagnesium iodide there was obtained *sym*.-dibenzyltetraethyl-disiloxane (79 per cent), b.p., 318–320°/735 mm.;  $d_4^{20}$  0.9991;  $n_D^{20}$  1.5209;  $MR_D$ , calcd. 97.20;  $MR_D$ , found 97.01.

Bromination of trimethylbenzylsilane gave benzyl bromide; whereas nitration gave phenylnitromethane.

Triethylchlorosilane and ethyl sodioacetoacetate gave ethyl  $\beta$ -triethylsiloxycrotonate (61 per cent), b.p., 108–110°/6 mm.;  $d_4^{20}$  0.9590;  $n_D^{20}$  1.4560;  $MR_D$ , calcd. 69.12;  $MR_D$ , found 69.42.

These variously substituted  $\beta$ -lactams of  $\beta$ -anilino- $\beta$ -phenylpropionic acid were prepared by using the general procedure of Gilman and Speeter<sup>2</sup>:  $\beta$ -lactam of  $\beta$ -anilino- $\beta$ -*p*-anisylpropionic acid (25 per cent), m.p. 154–155.5°;  $\beta$ -lactam of  $\beta$ -*p*-chloroanilino- $\beta$ -*o*-chlorophenylpropionic acid (38 per cent), m.p. 129–130°;  $\beta$ -lactam of  $\beta$ -*p*-chloroanilino- $\beta$ -*p*-anisylpropionic acid (36 per cent), m.p. 108–109°;  $\beta$ -lactam of  $\beta$ -*m*-chloroanilino- $\beta$ -*p*-anisylpropionic acid (17.5 per cent), m.p. 110.5–112°;  $\beta$ -lactam of  $\beta$ -*p*-chloroanilino- $\beta$ -phenylpropionic acid (49.6 per cent), m.p. 110–111°;  $\beta$ -lactam of  $\beta$ -*p*-anisidino- $\beta$ -phenylpropionic acid (43 per cent), m.p. 96°;

<sup>2</sup> Gilman and Speeter, Jour. Am. Chem. Soc., 65, 2256 (1943).

and the  $\beta$ -lactam of  $\beta$ -anilino- $\beta$ -*o*-chlorophenylpropionic acid (34 per cent), m.p. 93–94°.

The  $\beta$ -lactam of  $\beta$ -anilino- $\beta$ -phenylpropionic acid was hydrolyzed by means of aqueous base (25 per cent) or acid (45 per cent); the product in both cases was  $\beta$ -anilino- $\beta$ -phenylpropionic acid, m.p. 134–135°.

An ethanol solution of the  $\beta$ -lactam of  $\beta$ -anilino- $\beta$ -phenylpropionic acid when treated with dry hydrogen chloride gave ethyl  $\beta$ -anilino- $\beta$ -phenylpropionate (85 per cent), m.p. 74–75°.

Nitration of 2-phenylpyridine<sup>a</sup> by the method of Forsyth and Pyman<sup>1</sup> gave a mixture of the 2-(nitrophenyl) pyridines which were separated according to the method of these investigators. 2-(4'-Nitrophenyl)pyridine was reduced by hydrogen and Raney nickel to 2-(4'-aminophenyl)pyridine (95 per cent), m.p. 97–98°.

2-(4'-Aminophenyl)pyridine with benzaldehyde gave 2'-(4'-benzalaminophenyl)pyridine (95 per cent), m.p. 102–103°; with salicylaldehyde, 2-(4'-salicylaminophenyl)pyridine (93 per cent), m.p. 137–138°; with acetonylacetone, 2-[4'-(2'',5''-dimethylpyrryl-1'')phenyl]pyridine, m.p. 98.5–99°; with formic acid, 2-(4'-formylaminophenyl)pyridine, m.p. 127–128°; and with acetic anhydride, 2-(4'-acetaminophenyl)pyridine (94 per cent), m.p. 134–135°.

Nitration of 2-(4'-acetaminophenyl)pyridine gave 2-(3'-nitro-4'-acetaminophenyl)pyridine (94 per cent), m.p. 142–143°. Basic hydrolysis of this product gave 2-(3'-nitro-4'-aminophenyl)pyridine (91 per cent), m.p. 148–149°. Action of formic acid in this latter product gave 2-(3'-nitro-4'-formylaminophenyl)pyridine (82 per cent), m.p. 148–149°.

2-(4'-Methoxyphenyl)pyridine<sup>b</sup> was hydrolyzed with hydrobromic acid to give 2-(4'-hydroxyphenyl)pyridine (90 per cent), m.p. 164–165°. Nitration of this product gave 2-(3'-nitro-4'-hydroxyphenyl)pyridine (88 per cent), m.p. 126–127°.

*p*-Bromothiophenol (37.5 per cent), m.p. 74–75°, was prepared by the action of potassium ethylxanthate upon a *p*-bromobenzenediazonium chloride solution. This product upon treatment with *n*-butyllithium gave *p*-mercaptophenyllithium; carbonation of this compound gave *p*-mercaptobenzoic acid (70 per cent), m.p. 213–215°. *p*-Mercaptophenyllithium reacted with pyridine to give 2-(4'-mercaptophenyl)pyridine (21 per cent), b.p. 190–193°/3 mm.

$\gamma$ -(*p*-Nitrophenyl)propyl chloride<sup>c</sup> reacted with diethylamine to give diethyl- $[\gamma$ -(*p*-nitrophenyl)propyl]amine (70 per cent), b.p., 145–146°/1 mm. This product was reduced with hydrogen and Raney nickel to give diethyl- $[\gamma$ -(*p*-aminophenyl)propyl]amine (92 per cent), b.p., 152–153°/2 mm.

The isomeric 2-nitrophenylpyridines, 3-nitrophenylpyridines, and 4-nitrophenylpyridines were synthesized by a modification of the method of Heilbron and co-workers<sup>d</sup>.

<sup>1</sup> J. T. Edward, unpublished studies.

<sup>a</sup> Forsyth and Pyman, Jour. Chem. Soc., 2912 (1926).

<sup>b</sup> Braun and Deutsch, Ber., 45, 2504 (1912).

<sup>d</sup> Haworth, Heilbron and Hey, Jour. Chem. Soc., 349 (1940)

2-(2'-Nitrophenyl)pyridine was reduced to the corresponding amine (89 per cent), b.p. 192-194°/1 mm. These derivatives of this amine were formed: 2-[2'-(2'',5''-dimethylpyrryl-1'')phenyl]pyridine, m. p. 101-102°; and 2-(2'-salicylaminophenyl)pyridine, m.p. 118-120°.

3-(2'-Nitrophenyl)pyridine was reduced to the corresponding amine (90 per cent), b.p. 210-212°/3 mm. This compound gave 3-[2'-(2'',5''-dimethylpyrryl-1'')phenyl]pyridine, m.p. 66-67°.

4-(3'-Aminophenyl)pyridine, m.p. 164-166°, 3-(3'-aminophenyl)pyridine, m.p. 77-78°, and 2-(3'-aminophenyl)pyridine, m.p. 72-73°, were prepared from the corresponding nitro-compounds.

2-(3'-Aminophenyl)pyridine gave 2-[3'-(2'',5''-dimethylpyrryl-1'')phenyl]pyridine, m.p. 83.5-84°, and 2-(3'-salicylaminophenyl)pyridine, m.p. 77-78°.

2,6-(4',4''-Diaminodiphenyl)pyridine, m.p. 216-218°, and 3-(4'-aminophenyl)pyridine, m.p. 116-118°, were prepared from their corresponding nitro-compounds. This latter product gave 3-[4'-(2'',5''-dimethylpyrryl-1'')phenyl]pyridine, m.p. 116-117°.

2-(2'-Nitro-4'-methoxyphenyl)pyridine (1.3 per cent), m.p. 89-90°, and 3(?)-(2'-nitro-4'-methoxyphenyl)pyridine (2.3 per cent), m.p. 66-67°, were prepared by the action of a 2-nitro-4-methoxybenzenediazonium chloride solution on pyridine.

Reduction of the 2-isomer gave 2-(2'-amino-4'-methoxyphenyl)pyridine (80 per cent), m.p. of dihydrochloride 199-200°.

2-(4'-Nitrophenyl)thiophene, prepared by a modification of the method of Gomberg and Bachman<sup>†</sup>, on reduction with hydrogen and Raney nickel gave 2-(4'-aminophenyl)thiophene, m.p. 69-71°. The position of the phenyl ring in the thiophene nucleus was proven by deamination of 2-(4'-aminophenyl)thiophene to the known 2-phenylthiophene.

<sup>†</sup> Gomberg and Bachman, Jour. Am. Chem. Soc., 46, 2339 (1924).

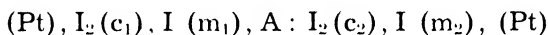
# THE REACTION OF IODINE WITH STARCH AND THE SCHARDINGER DEXTRINS<sup>1</sup>

HARVEY ALBERT DUBE

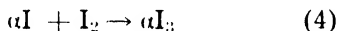
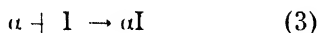
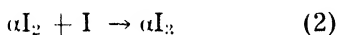
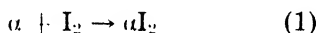
*From the Department of Chemistry, Iowa State College*

The reaction of iodine with amylose has been explained in terms of the helical theory. This investigation offers additional evidence to support the helical theory. The reaction of the Schardinger dextrans and iodine has been studied because of the similarity between the ring structure of the dextrans and the helical structure of the amylose molecule.

The reactions of iodine, iodide ion and the Schardinger dextrans were followed potentiometrically by measuring the E. M. F. of a cell of the type

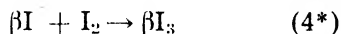


where A is the material studied. The results indicate that the following reactions occur in solution between cyclohexaamylose ( $\alpha$ -dextrin), iodine and iodide ion:



The equilibrium constants for these reactions are:  $K_1 = 2.0 \times 10^{-3}$ ,  $K_2 = 1.35 \times 10^{-5}$ ,  $K_3 = 13.5$ ,  $K_4 = 2.0 \times 10^{-7}$ . The crystalline complex formed between cyclohexaamylose and potassium iodide has been prepared. The constitution of the crystalline iodine complexes of cyclohexaamylose, which have previously been reported, agree with the above reactions.

An identical series of reactions with cycloheptaamylose ( $\beta$ -dextrin). The equilibrium constants for the reactions



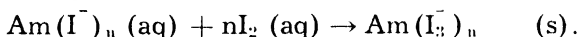
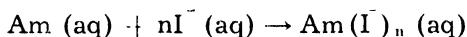
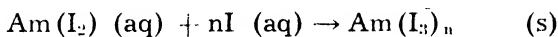
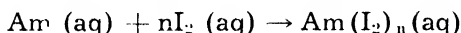
are  $K_3 = 1.45$  and  $K_4 = 1.0 \times 10^{-6}$ .

The results obtained with the Schardinger dextrans have been used to interpret the reactions between amylose, iodine and iodide ion. These

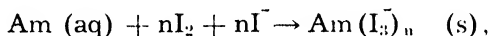
<sup>1</sup> Doctoral thesis No. 834, submitted February 11, 1947.



reactions were also studied potentiometrically. The characteristic behavior of the amylose-iodine complex is best explained by the series of reactions:



The effect of a change in the iodide concentration, amylose concentration, or iodine concentration is explained by the above reactions. The following thermodynamic quantities have been determined for the reaction,



per mole of iodine:

$$\Delta F^\circ_{298} = -12,000 \text{ cal. per mole of iodine}$$

$$\Delta S^\circ_{298} = -25.6 \text{ e. u. per mole of iodine}$$

$$\Delta H^\circ_{298} = -19,600 \text{ cal. per mole of iodine.}$$

The effect of chain length on the iodine activity of the amylose-iodine complex has been used as the basis for the development of a method of determining the chain length distribution of amylose. The weight-average distribution of amylose can be determined from a single potentiometric iodine titration. The method should be useful in determining the efficiency of fractionation procedures.

# THE QUANTITATIVE SPECTROGRAPHIC ANALYSIS OF THE RARE EARTH ELEMENTS<sup>1</sup>

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The limited application of ordinary chemical methods to the analysis of the rare earth group has resulted in the development of a number of physical and physico-chemical methods. None of the methods so far proposed have offered a practical means of performing the following analyses: (a) the determination of low concentrations of rare earth impurities in purified rare earths, and (b) the determination of major amounts of those members of the group which possess no absorption bands in the wavelength regions accessible by ordinary spectrophotometric apparatus. This investigation is concerned with development of emission spectra methods which are capable of yielding the analytical information mentioned above.

A Jarrell-Ash Wadsworth mounting 21-foot grating spectrograph was used. The complex spectra of the rare earths necessitated the use of the second order in which the linear dispersion was 2.5 Å/mm. The external optical system was designed to focus the source on the collimating mirror. A rotating stepped sector placed in front of the slit was used for intensity modulations. The plates were processed in an ARL-Dietert developing machine and photometric measurements were made on an ARL-Dietert comparator-densitometer. The calibration of the response of the Eastman Type III-O and Spectrum Analysis No. 1 emulsions was made by the two-step sector, preliminary curve method.

The logical choice of the chemical form of the samples for excitation was the ignited rare earth oxides since the samples from fractionation procedures are obtained either in this form or are readily converted to oxides. The refractory properties of the rare earth oxides restricted the type of excitation to the d-c arc, for it alone produced temperatures high enough to vaporize the oxides into the discharge zone. Since the erraticness and poor reproducibility of the d-c arc discharge greatly impairs the usefulness of this source for quantitative analysis, the plan of attack was to develop means of reducing and correcting for the large excitation variables.

It was found that d-c arcs of currents as high as 18 amperes did not provide electrode temperatures high enough to vaporize a sufficient amount of the rare earth oxides to maintain a stabilized arc. Following the suggestions of Bauer, a number of experiments were performed in which the rare earth oxides were mixed with metallic oxides of lower

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<sup>1</sup> Doctoral thesis No. 851, submitted June 9, 1947.

boiling points in the hope that the latter would support a stabilized arc and aid in transporting the rare earth oxides into the discharge zone during the stable arc period. These added oxides successfully stabilized the 17.3 ampere arc but moving-plate spectrograms taken during the excitation revealed that the major portion of the rare earths were actually volatilized and excited immediately preceding and during the unstable discharge following the stable period. A mixture of powdered graphite and rare earth oxides was found to produce a stabilized arc at 16 amperes or above. Moving-plate spectrograms of these arcings indicated uniform emission during the excitations. Apparently the more volatile rare earth metals were formed either by chemical reduction or by carbide formation followed by thermal decomposition of the latter. The optimum experimental conditions for this type of excitation were: current, 17.5 amperes; weight of electrode charge, 15 mg; type of electrode,  $\frac{1}{4}$ -inch diameter graphite with 2 mm-deep thin-walled cavity; composition of charge, 1:1 mixture of rare earth oxides and powdered graphite.

The internal standard technique was used to compensate for the residual excitation and photographic variables. In this technique it is assumed that concentration is a function of the single variable  $I_A/I_B$ , where  $I_A$  and  $I_B$ , respectively, are the line intensities of the element to be determined and the internal standard element. Accordingly, for greatest effectiveness, it was desirable to choose the internal standard and line pair so as to maintain a constancy of  $I_A/I_B$  during the excitation, regardless of changes in voltage, arc current, effective excitation temperature, distillation and other effects. In view of the similarity in the physical properties of the rare earths, the logical choice of the internal standard was a rare earth which was either present or could be introduced into a sample in a constant amount. For the determination of minor impurities in purified rare earths, this constant amount was provided by the major constituent whose concentration remained essentially constant. The selection of cerium as the internal standard for the analysis of complex mixtures was based on the relative ease with which tetravalent cerium could be separated from the rest of the rare earths. The presence of a constant rare earth concentration in mixtures for internal standard purposes was assured by first removing any cerium present and then reintroducing a standard amount. The following advantages were obtained by the addition of the cerium so that the final composition was 80 per cent ceric oxide and 20 per cent sample: (a) elimination of multiple cerium separations since the cerium remaining after the preliminary separation was negligible compared to the amount added, (b) elimination of the preliminary cerium separation when the original cerium concentration was low, (c) reduction of extraneous influences on the excitation conditions of large changes in sample compositions, and (d) reduction of self-reversal effects on the lines of the elements to be determined.

Insofar as possible, line pairs were selected whose components possessed equivalent excitation properties and intensities and proximity of wavelengths. The experimental determinations of constancy of intensity

ratios during the excitations were made by means of moving-plate spectrograms. The following mixtures were investigated: (a) neodymium oxide containing a small amount of samarium oxide; (b) samarium oxide containing a small amount of europium oxide; and (c) a mixture of equal amounts of yttrium and gadolinium oxide plus the added ceric oxide. The relatively small change in the intensity ratios for mixtures (b) and (c) approached the idealized condition seldom attained in d-c arc methods. For (a) the ratio change was greater but subsequent tests on reproducibility of the integrated ratio indicated an average deviation of 3 to 4 per cent and thus low enough for quantitative application.

The quantitative calibrations were performed by exposing synthetic standards under the optimum experimental conditions. The calibration curves were obtained by plotting the intensity ratios of the selected line pairs versus concentration on log-log paper. Calibrations were made for the following determinations: (a) minor amounts (0.1–4.0 per cent) of samarium in neodymium, (b) minor amounts (0.01–2.0 per cent) of europium in samarium, and (c) major amounts (10–100 per cent) of yttrium and gadolinium in complex mixtures.

The successful application of the internal standard principle was shown by the negligible effect on the intensity ratios of large variations in the experimental conditions. The results from a series of accuracy and precision determinations indicated an experimental error of 3.5 to 4 per cent.

The methods which were developed have low time and sample requirements per analysis and are readily adaptable to the analysis of purified rare earths and complex mixture.

# THE EFFECT OF CROP ROTATION ON SOIL AGGREGATION AND RELATED CHARACTERISTICS IN A BELINDA SILT LOAM SOIL<sup>1</sup>

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Soil aggregate studies were made on samples from 8 different rotations at the pasture farm near Albia, Iowa, located on Belinda silt loam soil. The rotation experiments were started in 1941. The eight types of rotations were as follows: corn-oats, corn-oats with sweet clover as catch crop, corn-oats-meadow, corn-oats-meadow-meadow, corn-corn-oats-meadow-meadow, corn—continuously with a sweet clover cover crop, corn-soybeans, and corn-corn-oats-meadow.

The seasonal variation and the effect of rotation on total aggregates, size distribution, aggregate stability and permeability may be summarized as follows:

In the 8 sampling dates from March, 1945 to September, 1946 the highest percentage of stable aggregates  $> .1$  mm. is from the sampling of August, 1945, the lowest being from that of March of the same year. The seasonal variation follows a regular trend for all sized fractions. In general, as the larger sized fraction decreased the smaller sized increased. For instance, from July to December in 1945 the largest fraction was high while the smallest fraction was low.

The low moisture content of the soil which followed a period of rapid decomposition of organic matter, in addition to the presence of rootlets from the rapidly growing crop are the important factors contributing to the high value of  $> .1$  mm. aggregates in August, 1945.

The moisture content at the time of sampling varied widely between dates and under different crops. This difference amounted to 50 per cent between the oats and clover plots and corn soybean plots in September, 1946, which undoubtedly, greatly affected the difference in size distribution of soil aggregates between these plots.

The effect of different rotations on total aggregates  $> .1$  mm. was in the order corn-oats-meadow-meadow  $>$  corn-corn-oats-meadow-meadow  $>$  corn-corn-oats-meadow  $>$  corn-oats with sweet clover catch crop  $>$  corn-oats  $>$  corn-soybean.

The effect of different rotations on size distribution of aggregates was very striking. In continuous grass plots the  $> 2$  mm. fraction predominates over the smaller sized aggregates, especially the smallest fraction of .25-.1 mm. A reverse condition was found for the other rotations; that is, the smallest fraction, .25-.1 mm., predominated over the  $> 2$  mm. fraction. A corn-oats-meadow-meadow rotation gave the highest percentage of  $> 2$  mm. fraction, whereas the reverse was true for the corn-soybean

<sup>1</sup> Doctoral thesis No. 835, submitted March 18, 1947.

rotation. There was an insignificant change in the 1-.5 and .5-.25 mm. fractions.

The crop grown for the current year as well as the intensity of the rotation affected the size distribution of aggregates, especially the  $> 2$  mm. and  $> 2-1$  mm. fractions.

The effect of an individual crop in the previous year on the size distribution of soil aggregates was also noticeable. For instance, the second year meadow in corn-oats-meadow-meadow rotation is much higher than that of the first year corn in corn-corn-oats-meadow rotation.

The total stable aggregates  $> .1$  mm. were increased by air drying. In spite of the fact that air drying caused a decrease in the  $> 2$  mm. and  $2-1$  mm. fractions, there was a sufficient increase in the .5-.25 mm. and the .25-.10 mm. fractions to account for a total increase in aggregates larger than .1 mm. In general, air drying helps to consolidate the smaller fractions and tends to break down the larger ones, partly at least, by weakening the binding strength of the fibrous rootlets that were present in soil, especially in the  $> 2$  mm. fraction.

Since the aggregates  $> 2$  mm. fraction as well as the finest aggregates .25-.1 mm. were both important factors in characterizing soil structure the ratio between these fractions was proposed as a valuable criterion in ranking the different rotations on the basis of development of desirable structure.

Different rotations as well as different crops on the land when the samples were taken affected greatly the stability of aggregates. A comparison of the April 4 and September 17, 1946 dates showed that the changes occurred in soil aggregation as the growing season advanced. For example, in the corn-oats-meadow rotation the stability factor under first year meadow on April 4, 1946 was .060; on September 17, when the meadow was in its second year the stability factor was .180.

A highly significant correlation coefficient of .99 was found between "stability factor" and permeability for samples of April 4 and also a highly significant correlation coefficient of .90 was found for the samples of September 17, 1946. The determination of "stability factor" and permeability was made on the  $2-1$  mm. fraction. It was thus concluded that permeability was closely related to stability of individual aggregates.

The highest carbon dioxide evolution was found under grass regardless of sampling dates. The lowest was found under corn-oats and corn-soybean rotations.

The organic carbon content under grass or corn-meadow rotations was higher than that under corn-soybean rotation. It was concluded that the high carbon dioxide evolution and the high organic carbon content in samples from grass or meadow plots were closely related to the high percentage of total stable aggregates  $> .1$  mm., which in turn was the result of a higher percentage of the  $> 2$  mm. and  $2-1$  mm. fractions in the soil under grass or meadow.

The volume of roots from the surface 6 inches of soil under different grasses was in the order Kentucky blue grass  $>$  timothy  $>$  big blue stem

> orchard grass > brome grass > red top. This was not in agreement with data reported by some investigators that showed an appreciably higher volume of roots under brome grass than under Kentucky blue grass. It was also of particular interest to note that while the red top had the lowest volume of grass roots the soil under red top contained the highest percentage of stable aggregate. In contrast with this the Kentucky blue grass, which had the highest volume of grass roots was found to have the lowest value of stable soil aggregates. No relationship was found between the dry weight of grass roots and the percentage of stable aggregate > .1 mm. .

# SOME SUBSTITUTED ALKYLAMINO SULFIDES AND SULFONES<sup>1</sup>

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A brief survey of the compounds used in the treatment of malaria and tuberculosis has been given with some discussion of their properties. In order to obtain some compounds which would be of therapeutic value, a large number of compounds containing sulfur, as sulfides and sulfones, has been prepared. The reasons for the use of sulfur-containing compounds as therapeutic agents have been given and the mechanisms of some of the reactions discussed.

A series of sulfur derivatives of chalcones was prepared by reacting diethylaminoalkyl mercaptans and thiols with various substituted chalcones. The condensations involving the dialkylaminoalkyl mercaptans were made by reacting the amine as the hydrochloride. The thiols were condensed under basic conditions. The mechanism of the reaction which is probably 1,4-addition has been discussed. The following compounds were prepared:  $\beta$ -(2-diethylaminoethylmercapto)- $\beta$ -phenylpropiophenone hydrochloride, m.p. 113–15°;  $\beta$ -(3-diethylaminopropylmercapto)- $\beta$ -phenylpropiophenone methiodide, m.p. 112–13°; *p*-methoxy- $\beta$ -(2-diethylaminoethylmercapto)- $\beta$ -(*p*-dimethylaminophenyl)propiophenone hydrochloride, m.p. 145–6°; *p*-chloro- $\beta$ -(2-diethylaminoethylmercapto)- $\beta$ -(*p*-dimethylaminophenyl)propiophenone hydrochloride, m.p. 142–3°; 4-dimethylamino-4'-acetaminochalcone, m.p. 202–3°; *p*-acetamino- $\beta$ -(2-diethylaminoethylmercapto)- $\beta$ -(*p*-dimethylaminophenyl)propiophenone hydrochloride, m.p. 153–4°; 2-chloro-4'-acetaminochalcone, m.p. 167°; *p*-acetamino- $\beta$ -(*p*-tolylmercapto)- $\beta$ -(*o*-chlorophenyl)propiophenone, 148–9°; *p*-acetamino- $\beta$ -(*p*-tolylmercapto)- $\beta$ -(*p*-methoxyphenyl)propiophenone, m.p. 130–1°.

The reaction of mercaptans with unsymmetrical epoxides has been reviewed and the mechanism of the reaction discussed. A structure proof has also been made to show that the cleavage of unsymmetrical epoxides with mercaptans in a basic medium results in the formation of the  $\beta$ -hydroxyethyl sulfide. The  $\beta$ -hydroxyethyl sulfides prepared in this manner were patterned after the physiologically active epinephrine and ephedrine. The compounds prepared in this series were methyl  $\beta$ -phenyl- $\beta$ -hydroxyethyl sulfide, b.p., 127°/0.8 mm.; methyl  $\beta$ -phenyl- $\beta$ -hydroxyethyl sulfide methiodide, m.p. 138–9° (decomp.); methyl phenacyl sulfide, b.p. 130–2°/0.8 mm.; methyl phenacyl sulfide 2,4-dinitrophenylhydrazone, m.p. 164–5.5°;  $\gamma$ -diethylaminopropyl phenacyl sulfide, b.p. 158–60°/0.8 mm.;  $\gamma$ -diethylaminopropyl phenacyl sulfide 2,4-dinitrophenylhydrazone, m.p. 183–4°;  $\gamma$ -diethylaminopropyl  $\beta'$ -phenyl- $\beta'$ -hydroxyethyl sulfide, b.p. 149–52°/0.5 mm.;  $\beta$ -diethylaminoethyl  $\beta'$ -phenyl- $\beta'$ -hydroxyethyl sulfide,

<sup>1</sup> Doctoral thesis No. 814, submitted August 26, 1946.



b.p. 132°/0.5 mm.;  $\gamma$ -( $\beta$ -diethylaminoethylmercapto)propyl  $\beta'$ -phenyl- $\beta'$ -hydroxyethyl ether, b.p. 180–2°/1.5 mm.;  $\gamma$ -diethylaminopropyl  $\gamma'$ -diethylamino- $\beta'$ -hydroxypropyl sulfide, b.p. 131–4°/0.5 mm.;  $\beta$ -diethylaminoethyl  $\gamma'$ -diethylamino- $\beta'$ -hydroxypropyl sulfide, b.p. 121–2°/0.8 mm.;  $\gamma$ -diethylamino- $\beta$ -hydroxypropyl phenyl sulfide, b.p. 125–8°/0.5 mm.;  $\gamma$ -diethylamino- $\beta$ -hydroxypropyl *p*-dimethylaminophenyl sulfide, b.p. 145–7°/0.001 mm.;  $\gamma$ -diethylamino- $\beta$ -hydroxypropyl *p*-tolyl sulfide, b.p. 137°/0.8 mm.;  $\gamma$ -diethylamino- $\beta$ -hydroxypropyl *p*-aminophenyl sulfide, b.p. 153°/1 mm.;  $\gamma$ -diethylamino- $\beta$ -hydroxypropyl *p*-chlorophenyl sulfide, b.p. 149–52°/1.5 mm.;  $\gamma$ -diethylamino- $\beta$ -hydroxypropyl *p*-tolyl sulfone, b.p. 217°/1 mm.; *p*-aminophenyl  $\beta$ -phenyl- $\beta$ -hydroxyethyl sulfide, b.p. 185°/0.001 mm.;  $\gamma$ -diethylaminopropyl  $\beta'$ -hydroxy- $\Delta^3$ -butenyl sulfide, b.p. 123°/0.8 mm.;  $\beta$ -diethylaminoethyl  $\beta'$ -hydroxy- $\Delta^3$ -butenyl sulfide, b.p. 111°/1.5 mm.; *p*-aminophenyl  $\beta$ -hydroxy- $\Delta^3$ -butenyl sulfide, b.p. 165–8°/0.8 mm.;  $\beta$ -diethylaminoethyl  $\beta'$ -phenyl- $\beta'$ -hydroxyethyl ether, b.p. 142–4°/0.5 mm.;  $\beta$ -diethylaminoethyl  $\beta'$ -phenyl- $\beta'$ -acetoxylethyl ether, b.p. 138–41°/0.5 mm.

A group of quinoline sulfides has been prepared by reacting alkyl mercaptides with chloroquinolines. The following new compounds were prepared: 7-chloro-4-quinolyl 4'-methyl-2'-thiazolyl sulfide hydrochloride, m.p. 169–70°; 7-chloro-4-quinolyl  $\beta$ -hydroxyethyl sulfide, m.p. 113–15°; 7-chloro-4-quinolyl  $\beta$ -chloroethyl sulfide hydrochloride, m.p. 196–7°; 7-chloro-4-quinolyl  $\beta$ -chloroethyl sulfide, m.p. 107–8°; 7-chloro-4-quinolyl  $\beta$ -( $\gamma'$ -diethylaminopropylmercapto)ethyl sulfide dihydrochloride, m.p. 176–7°; 7-chloro-4-quinolyl  $\beta$ -(4'-methyl-2'-thiazolylmercapto)ethyl sulfide hydrochloride, m.p. 205–8°.

The antimalarial activity of  $N^1$ -*p*-chlorophenyl- $N^3$ -isopropylbiguanide suggested an investigation of the physiological activity of some sulfur and oxygen analogs of this compound. Thus the following were prepared: 1-*p*-chlorophenyl-2-thiolmethylpseudothioureia hydroiodide, m.p. 165–7°; 1-*p*-chlorophenyl-5-isopropylidithiobiuret, m.p. 135–7°; 1,5-di(*p*-chlorophenyl)-2-thiolmethylpseudodithiobiuret, m.p. 154–5°; 1,5-di(*p*-chlorophenyl)dithiobiuret, m.p. 168°; 1-*p*-chlorophenyl-2-thiolmethyl-5-phenylpseudomonothiobiuret, m.p. 153–4°; 1-*p*-chlorophenyl-5-phenyl-2-monothiobiuret, m.p. 163–5°; 1-*p*-chlorophenyl-2-thiolmethyl-5-methylpseudomonothiobiuret, m.p. 160–1°; 1-*p*-chlorophenyl-5-methyl-2-monothiobiuret, m.p. 182–3°.

In connection with various studies on the preparation of some pharmacologically active compounds the following new compounds were prepared:  $\gamma$ -(*p*-nitrophenoxy)propyl  $\beta$ -morpholinoethyl sulfone, m.p. 98–9°;  $\gamma$ -(*p*-aminophenoxy)propyl  $\beta$ -morpholinoethyl sulfone, m.p. 117°;  $\gamma$ -(*p*-isopropylaminophenoxy)propyl  $\beta$ -morpholinoethyl sulfone (?), m.p. 106–8°;  $\beta$ -hydroxyethyl 2-pyridyl sulfide picrate, m.p. 113–14°;  $N$ - $\gamma$ -diethylaminopropyl-3-methoxy-6-bromoaniline picrate, m.p. 116–17°;  $N$ - $\gamma$ -diethylaminopropyl-*o*-bromoaniline dihydrochloride, m.p. 171–3°; 2-morpholinoquinoline, m.p. 164°; 6-methoxy-2-morpholinoquinoline, m.p. 102–3°; 9-[*p*-(2',5'-dimethylpyrryl-1')phenyl]acridine, m.p. 145–7°; *p*-methoxy-*p'*-acetaminobenzophenone, m.p. 170–1°; *p*-methoxy-*p'*-amino-benzophenone, m.p. 121–2°.

# MECHANISMS OF ADDITION OF ORGANOLITHIUM COMPOUNDS TO QUINOLINE AND ISOQUINOLINE<sup>1</sup>

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A general review of the literature concerning the reaction of organo-metallic compounds with pyridine, quinoline, isoquinoline and acridine has been made. Their relationship to the ammonia system has been indicated and the mechanisms of addition of organolithium compounds to such cyclic ammono aldehyde ethers has been discussed. In the course of these studies, a new reaction, namely the addition of organolithium compounds to examples of a cyclic ammono ketone ether, (2-phenylquinoline), has been indicated. This reaction resulted in the preparation of a new type of compound, namely the 2,2-disubstituted-1,2-dihydroquinolines.

A series of 6-quinolyl and substituted 6-quinolyl nitro-, amino-, and acetamidophenyl sulfides and sulfones has been synthesized and submitted for testing for antimalarial and tuberculocidal activity.

One equivalent of *p*-bromoaniline was reacted with three equivalents of *n*-butyllithium. To the insoluble lithium salt of *p*-aminophenyllithium was added two equivalents of quinoline. Subsequent to hydrolysis, nitrobenzene oxidation of the intermediate dihydro product, and distillation, a glass (70 per cent), b.p. 165°–175° (0.005 mm.), was obtained. The picrate was formed and found to be a mixture. By means of the higher solubility in benzene of the picrate of a secondary product of reaction, the insoluble picrate of 2-(*p*-aminophenyl)-quinoline was obtained in pure form as the residue. Decomposition of the picrate with dilute ammonium hydroxide gave 2-(*p*-aminophenyl)-quinoline, m.p. 138°–138.5°; picrate, m.p. 197°–198°. The analyses for the secondary product of reaction most nearly corresponded to those required for *x*-butyl-*x*-(*p*-aminophenyl)-quinoline, m.p. 148°–148.5°; picrate, m.p. 220°–221°. Condensation of 2-(*p*-aminophenyl)-quinoline with salicylaldehyde at 150° gave a quantitative yield of 2-(*p*-salicylideneaminophenyl)-quinoline, m.p. 188°–188.5°.

Addition of phenyllithium to 2-phenylquinoline after refluxing and stirring for twelve hours yielded a glassy distillate, b.p. 155°–165° (0.02–0.03 mm.). The product formed an insoluble hydrochloride (35 per cent) in dilute hydrochloric acid, by which means the compound was separated from the soluble 2-phenylquinoline present in small amount. The hydrochloride was decomposed with 10 per cent sodium hydroxide. Charcoaling and crystallization gave 2,2-diphenyl-1,2-dihydroquinoline, m.p. 86°–87°. To establish the fact that 1,2-addition had occurred, 2-phenyl-2-(*p*-tolyl)-1,2-dihydroquinoline was prepared by the same reaction using different starting materials. Thus, *p*-tolyllithium was added to 2-phenylquinoline,

<sup>1</sup> Doctoral thesis No. 821, submitted December 16, 1946.

and phenyllithium was added to 2-(*p*-tolyl)-quinoline. The products from each reaction, namely 2-phenyl-2-(*p*-tolyl)-1,2-dihydroquinoline, melted at 86°–87° and were identical (mixed m.p.).

2-(*o*-Biphenyl)-quinoline (50 per cent) was prepared by addition of *o*-biphenyllithium to quinoline; b.p. 162°–166° (0.007 mm.), m.p. 102°–103°. 2-(*p*-Biphenyl)-quinoline, m.p. 178°–179°, was prepared by the reaction of *p*-biphenyllithium with quinoline.

5-Aminoisoquinoline and an excess of acetylacetone when refluxed two hours, gave 5-(2,5-dimethyl-1-pyrryl)-isoquinoline (95 per cent), m.p. 83°–84°; picrate, m.p. 174°–175°. Condensation of 4-aminoisoquinoline and acetylacetone by refluxing three hours gave 4-(2,5-dimethyl-1-pyrryl)-isoquinoline (97 per cent), m.p. 77°–78°. 6-Aminoquinoline, when condensed with acetylacetone gave 6-(2,5-dimethyl-1-pyrryl)-quinoline (93 per cent), m.p. 98°–99°; picrate, m.p. 185°–186°.

Addition of *p*-dimethylaminophenyllithium to isoquinoline in ether gave, subsequent to hydrolysis with water, nitrobenzene oxidation, and distillation, 1-(*p*-dimethylaminophenyl)-isoquinoline (55 per cent), b.p. 196°–199° (4 mm.), m.p. 114.5°–115°; picrate, m.p. 220°–221°. By the same procedure *p*-tolyllithium and isoquinoline gave 1-(*p*-tolyl)-isoquinoline (55 per cent), b.p. 174°–183° (5 mm.); m.p. 71°–72°. Similar addition of *p*-(2,5-dimethyl-1-pyrryl)-phenyllithium to isoquinoline yielded 1-[*p*-(2,5-dimethyl-1-pyrryl)-phenyl]-isoquinoline (45 per cent), b.p. 203°–208° (4 mm.); m.p. 159°–160°. 1-(*p*-Anisyl)-5-(2,5-dimethyl-1-pyrryl)-isoquinoline (38 per cent), b.p. 222°–228° (2 mm.), was obtained from the interaction of *p*-anisyllithium and 5-(2,5-dimethyl-1-pyrryl)-isoquinoline. From the reaction between 5-(2,5-dimethyl-1-pyrryl)-isoquinoline and *p*-(2,5-dimethyl-1-pyrryl)-phenyllithium, 1-[*p*-(2,5-dimethyl-1-pyrryl)-phenyl]-5-(2,5-dimethyl-1-pyrryl)-isoquinoline (31 per cent), b.p. 220°–230° (0.05 mm.); m.p. 214°–215° was obtained.

1-(*p*-Nitrophenyl)-isoquinoline (60 per cent), m.p. 155°–156°, was prepared by dehydrogenation of 1-(*p*-nitrophenyl)-3,4-dihydroisoquinoline, with use of palladium black. 1-(*p*-Aminophenyl)-isoquinoline (70 per cent), m.p. 191°–192°, was prepared by reduction of 1-(*p*-nitrophenyl)-isoquinoline with hydrogen in the presence of Raney nickel. The same compound (mixed m.p.) was prepared (70 per cent) by the addition of the lithium salt of *p*-aminophenyllithium (obtained by halogen-metal interconversion of *p*-bromoaniline with *n*-butyllithium) to isoquinoline as described under 2-(*p*-aminophenyl)-quinoline. By the same means, 1-(*p*-mercaptophenyl)-isoquinoline hydrochloride was prepared by the addition of the lithium salt of *p*-mercaptophenyllithium to isoquinoline. Subsequent to hydrolysis, alkaline extraction, acidification with acetic acid and ether extraction, the hydrochloride (20 per cent) was precipitated with ethereal hydrogen chloride, m.p. 271°–272°. Carbonation of an aliquot of the lithium salt of *p*-mercaptophenyllithium gave *p*-mercaptobenzoic acid (75 per cent), m.p. 214°–215°.

6-Quinolyl *p*-nitrophenyl sulfone (67 per cent), m.p. 181°–182°, was prepared by the Skraup synthesis applied to 4-nitro-4'-aminodiphenyl

sulfone (or the acetamido compound) using the arsenic oxide modification.<sup>2</sup> Reduction with hydrogen (Raney nickel catalyst) gave 6-quinolyl *p*-aminophenyl sulfone (88 per cent), m.p. 178°–179°. A similar Skraup synthesis gave 6-quinolyl *p*-nitrophenyl sulfide (55 per cent), m.p. 168.5°–169.5°. 6-Quinolyl *p*-aminophenyl sulfide dihydrochloride (78 per cent), m.p. 217°–218°, was prepared by reduction of the latter as given above, and the product was converted to the hydrochloride with ethanolic hydrogen chloride.

*p*-Aminothiophenol (69 per cent), b.p. 143°–146° (17 mm.), m.p. 43°–45°, was prepared by the interaction of *p*-chloronitrobenzene and aqueous sodium sulfide. 5-Nitro-6-chloroquinoline and the sodium salt of *p*-aminothiophenol gave 5-nitro-6-quinolyl *p*-aminophenyl sulfide (90 per cent), m.p. 137°–138°. Reduction with hydrogen in the presence of Raney nickel, and conversion to the hydrochloride gave 5-amino-6-quinolyl *p*-aminophenyl sulfide trihydrochloride (88 per cent), m.p. 261°–262°. 5-Nitro-6-chloroquinoline and the sodium salt of *p*-acetamidothiophenol gave 5-nitro-6-quinolyl *p*-acetamidophenyl sulfide (80 per cent), m.p. 173°–174°. The compound was also obtained by acetylation of 5-nitro-6-quinolyl *p*-aminophenyl sulfide. Condensation of the sodium salt of *p*-chlorothiophenol and 5-nitro-6-chloroquinoline gave 5-nitro-6-quinolyl *p*-chlorophenyl sulfide (88 per cent), m.p. 115°–116°.

From the reaction of the sodium salt of *p*-acetamidobenzenesulfinic acid and 5-nitro-6-chloroquinoline, 5-nitro-6-quinolyl *p*-acetamidophenyl sulfone (quantitative yield), m.p. 247°–248°, was obtained. Deacetylation with boiling dilute hydrochloric acid gave 5-nitro-6-quinolyl *p*-aminophenyl sulfone (quantitative yield), m.p. 258°–259°. 5-Nitro-8-acetamido-6-quinolyl *p*-acetamidophenyl sulfone (92 per cent), m.p. 313°–314°, resulted from the reaction of 5-nitro-6-chloro-8-acetamidoquinoline<sup>3</sup> and sodium *p*-acetamidobenzenesulfinate. Deacetylation with boiling dilute hydrochloric acid and neutralization gave 5-nitro-8-amino-6-quinolyl *p*-aminophenyl sulfone (91 per cent), m.p. 247°–247.5°. Condensation of 5-nitro-6-chloro-8-aminoquinoline<sup>3</sup> with sodium *p*-acetamidobenzenesulfinate gave 5-nitro-8-amino-6-quinolyl *p*-acetamidophenyl sulfone (95 per cent), m.p. 261.5°–262.5°.

Oxidation of  $\gamma$ -(*p*-nitrophenoxy)-propyl  $\beta$ -hydroxyethyl sulfide<sup>4</sup> by hydrogen peroxide in glacial acetic acid medium yielded the corresponding sulfone (85 per cent), m.p. 103°–104°, together with a small amount of the acetoxy compound, m.p. 85°–86°. The crude sulfone was therefore refluxed with 2N sulfuric acid to hydrolyse the ester. The acetoxy compound was prepared (quantitative yield) either by acetylation of the pure  $\gamma$ -(*p*-nitrophenoxy)-propyl  $\beta$ -hydroxyethyl sulfone or by acetylation of the sulfide previous to oxidation (80 per cent). Reduction of the  $\gamma$ -(*p*-nitrophenoxy)-propyl  $\beta$ -hydroxyethyl sulfone with hydrogen (Raney

<sup>2</sup> Richter and Smith, Jour. Amer. Chem. Soc., 66, 397 (1944).

<sup>3</sup> Gilman, Benkeser, Gainer, Lindblad, Marshall, Massie, Myers, and Tolman, Jour. Amer. Chem. Soc., 68, 1577 (1946).

<sup>4</sup> Gilman and Fullhart, Jour. Amer. Chem. Soc., 67, 1585 (1945).

nickel) gave  $\gamma$ -(*p*-aminophenoxy)-propyl  $\beta$ -hydroxyethyl sulfone (92 per cent), m.p. 133.5°–134°. The latter compound, when added to ice-cold thionyl chloride, gave, on warming and subsequent decomposition of excess thionyl chloride with absolute ethanol,  $\gamma$ -(*p*-aminophenoxy)-propyl  $\beta$ -chloroethyl sulfone hydrochloride (78 per cent), m.p. 179°–180°.

Condensation of 6-methoxy-8-aminoquinoline with  $\gamma$ -chloropropyl mercaptan at 130°–135° for sixteen hours gave [subsequent to acid extraction, basic extraction (sodium hydroxide), acidification, neutralization (ammonium hydroxide) and ether extraction, followed by distillation] an oil (32 per cent), b.p. 174°–178° (0.5 mm.); hydrochloride, m.p. 172°–173.5°.

From the reaction of 4-bromoisquinoline and sodium hydroxide in the presence of copper bronze powder and copper sulfate, heated to 210° for twelve hours in a bomb chamber, 4-hydroxyisoquinoline was obtained (61 per cent), m.p. 223°; picrate, m.p. 243°–244°.

# FIELD INVESTIGATION OF CALCIUM ARSENATE, LEAD ARSENATE, AND SPREADING AGENTS FOR CODLING MOTH SPRAYS, AND AN ABRIDGED FORM OF CHI-SQUARE<sup>1</sup>

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When this investigation was undertaken (1939) the predominate codling moth insecticide was lead arsenate. An attempt was made to find a substitute which was cheaper and did not leave as toxic a residue on apples. As calcium arsenate seemed to offer fair promise of effectiveness in Iowa, it received first consideration as a substitute. Calcium arsenate was compared directly with lead arsenate in a commercial apple orchard near Mitchellville, Iowa. The experimental design consisted of 4 single row plots in each of 4 randomized blocks, which was duplicated in another section of the orchard. Two plots of each block were sprayed with calcium arsenate mixtures; the other two with lead arsenate mixtures. Two hundred apples from each of 6 randomly selected count trees were examined for codling moth injury 3 times during the season. The last count was made just prior to harvest.

The results of this experiment, augmented by the work of other experimenters, indicated that, in general, lead arsenate was superior to calcium arsenate as an insecticide for the codling moth. Calcium arsenate, however, could generally be depended upon for controlling the first brood codling moth in Iowa. The use of lead arsenate was indicated for heavy first brood infestations and for moderate to heavy second brood infestations.

As the use of spreading agents in codling moth sprays was questionable they were included in the investigation. In 1939 soybean flour was tested. In 1940 soybean flour, lime-casein and a sodium oleyl sulfate-resin type of spreader-sticker were tested. Conclusive results for soybean flour and lime-casein were obtained in that neither affected the efficacy of lead arsenate as a codling moth insecticide under Iowa conditions. Although no advantage was detected in this test, some advantage in the use of the sodium oleyl sulfate-resin spreader-sticker might be shown by more extensive studies. It can be concluded that the improvement of the physical properties of a spray mixture is not necessarily accompanied by increased insecticidal effect.

In evaluating the effectiveness of insecticides the investigator has need of a criterion of effect. Several different criteria have been used in the evaluation of codling moth damage to apples, but little was known concerning their relative merits. In order to increase the information

<sup>1</sup> Doctoral thesis No. 841, submitted May 26, 1947.

known about this subject it was included in the investigation. In the 1939 season 40 apples from each of 6 trees of each plot were cut open and examined for the number of injured fruit, worms, stings and injuries (worms + stings). In the 1940 season 25 apples from each of 4 trees of each plot of the section containing uniform trees were examined for wormy fruit, stung fruit, injured fruit, worms, stings and injuries (worms + stings). The results of these examinations indicated that satisfactory comparisons of different treatments in field experiments could be made on the basis of the number of injured fruit or the number of wormy fruit. Other criteria would be useful in making more detailed studies. An index number based on the use of the ratio of worms to stings was also tested and proved to be unreliable.

The relationship between the number of injuries and the number of injured fruit and between the number of worms and the number of wormy fruit can be expressed by the general equation

$$Y = aX^b.$$

Using the 1939 data the regression of the number of injuries per injured fruit was found to be

$$Y = 1.555X^{0.9942}.$$

From the 1940 data the number of injuries per injured fruit was expressed by

$$Y = 0.0105X^{2.9492}.$$

From the 1940 data the number of worms per wormy fruit was computed to be

$$Y = 1.112X^{1.2694}.$$

Hansberry obtained

$$Y = 1.049X^{1.1096}$$

for the equation of the number of worms per 100 apples based on percentage of wormy apples from data taken at Wenatchee, Washington in 1932 and 1933. These equations can be useful in converting data from one criterion to another, but they differ with season and locality which must be considered when they are employed.

The chi-square equation is useful in testing differences in laboratory comparisons of insecticides. The time consuming calculations involved are a drawback to its use in extensive studies. A simplified equation, based on the fourfold table, for determining the value of chi-square when there is one degree of freedom and the sample size is constant follows:

$$X^2 = \frac{2k(a - c)^2}{(a + c)(b + d)}.$$

Its use is limited by the requirement of a constant sample size, but in

laboratory experiments the samples are usually of uniform size. In order to incorporate Yates' correction for continuity the equation is changed to

$$X^2 = \frac{2k(|a - c| - 1)^2}{(a + c)(b + d)}.$$

The first of these two equations can be employed in constructing a table of fiducial limits. If the terms in it are rearranged with respect to  $c$  the following is formed:

$$(2k + X^2)c^2 - 2(2ka + bX^2)c + a[a(2k + X^2) - 2kX^2] = 0.$$

When  $P = 0.05$  the value of  $X^2 = 3.841$ . This value can be substituted for  $X^2$  to obtain

$$(2k + 3.841)c^2 - 2(2ka + 3.841b)c + a[a(2k + 3.841) - 7.682k] = 0$$

which is in the form of the general quadratic equation. If values are substituted for  $a$ , two values for  $c$  can be determined for each substitution. These values will form the limits of significance when  $P = 0.05$ . For Yates' correction for continuity to be included the values of  $a$  that are substituted should vary by 0.5. The values that are then obtained will have to be changed by 0.5 to obtain the proper fiducial limits. These limits can then be arranged in tabular form. For the proper functioning of such a table the sample size must be constant.



# ECOLOGICAL FACTORS AFFECTING THE ACTIVITY OF THE WESTERN FOX SQUIRREL, *SCIURUS NIGER* *RUFIVENTER* (GEOFFROY)<sup>1</sup>

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The purpose of this investigation was to measure certain attributes of weather and time, and to determine if they have any effects upon the fox squirrel by using the degree of its activity as a gauge of effects. By associating these effects with those caused by biological agents and other physical factors, a more thorough understanding of the ecology and management of the fox squirrel can be obtained.

The area chosen for the investigation consists of approximately 250 acres located along Squaw Creek, its tributary, Onion Creek, and the vicinity nearby in Sections 29, 32 and 33 of Franklin Township, Story County, Iowa. Floodplain and upland are the major topographic types.

Measurement of squirrel activity was obtained by using two count methods. The linear count consists of recording the number of squirrels seen as the worker walks a course of estimated length and width. The spot count or time-area count consists of recording the number of squirrels seen as the worker remains at a certain spot for a definite length of time. The following data were recorded during each count attempt for either of the two count methods: date, time of day in the field, degree of overcast, number of squirrels seen, time at which squirrels were seen, locality (ridge, ravine, floodplain) on which squirrels were seen, distance walked during observations, acreage observed, per cent of defoliation, count method used, and supplementary remarks such as presence and depth of snow, presence of precipitation (rain, snow, sleet, hail, mist, fog), foraging and feeding activity especially in cultivated tracts, mating actions, nest-building activity, play and animality traits. Readings of temperature, relative humidity, barometric pressure, precipitation and wind velocity were obtained for each count attempt.

The data for each ecological factor were analyzed separately to reveal whatever effects it might have upon squirrel activity. At the same time, cognizance was taken of the complex coactions exhibited by two or more ecological factors operating simultaneously.

Magnitude of fox squirrel activity in Iowa fluctuates with the seasons. Activity is greater in autumn than in any other season, and it is least in spring and summer. December shows the most intense activity and July has the least.

The fox squirrel is diurnal. It is seldom active before sunrise or after sunset. By hourly segregation most activity occurs from 7:00 A.M.

<sup>1</sup> Doctoral thesis No. 845, submitted June 6, 1947.

to 8:00 A.M. Least daytime activity occurs from 2:00 P.M. to 5:00 P.M. There are three peaks of activity throughout the day. The first is from 6:00 A.M. to 9:00 A.M. The second is from 11:00 A.M. to 1:00 P.M. The third and minor peak is from 6:00 P.M. to 7:00 P.M.

Activity in winter is greatest from 8:00 A.M. to 9:00 A.M. and from 12:00 M. to 2:00 P.M. It is least from 2:00 P.M. to 5:00 P.M. Spring activity is greatest from 6:00 A.M. to 11:00 A.M. and is least from 2:00 P.M. to 4:00 P.M. Greatest activity in summer occurs from 6:00 A.M. to 7:00 A.M. and from 6:00 P.M. to 7:00 P.M. Least activity occurs from 4:00 A.M. to 6:00 A.M., from 3:00 P.M. to 5:00 P.M. and from 7:00 P.M. to 8:00 P.M. Activity in autumn is most intense from 6:00 A.M. to 9:00 A.M. and from 11:00 A.M. to 12:00 M. It is least from 5:00 A.M. to 6:00 A.M. and from 5:00 P.M. to 6:00 P.M.

Seasonal variations of activity intensity during a day are the results of interactions of several factors. Excessive summer heat, welcome winter heat, and plentiful food supplies in autumn are important examples.

The fox squirrel is most active at temperatures ranging between forty degrees Fahrenheit and forty-nine degrees Fahrenheit. Temperatures at which activity is least are those from fifteen to nineteen degrees Fahrenheit and from seventy to eighty-four degrees Fahrenheit.

Data indicate that the fox squirrel is active in all temperatures of natural environment. However, at temperatures of ninety degrees Fahrenheit and above, it does display unmistakable lethargy. Under such temperature conditions the fox squirrel appears inclined to exert itself as little as possible. Extremely low temperatures by themselves do not retard squirrel activity as much as do high temperatures. However, low temperatures associated with other meteorological factors such as high wind, complete overcast or driving snow restrict movement very noticeably.

Fox squirrel activity is not dependent solely upon temperature fluctuations. In several instances consecutive mean hourly temperatures of approximately equal value were not accompanied by respective similar amounts of activity.

Greatest activity occurs at relative humidities between fifty and fifty-nine per cent and between eighty and ninety-nine per cent. Least activity occurs at relative humidities from twenty per cent to thirty-nine per cent. It is not known to what extent relative humidity *per se* modifies squirrel activity. Much activity occurs in early morning and early forenoon when relative humidities are often high. However, time of day and temperature as well as humidity are comparably important influences.

Wind velocity is one of the most influential environmental factors affecting squirrel activity. Magnitude of activity is inversely proportional to wind velocity. Of all environmental influences considered, the effects of wind are least interrelated with the effects of other factors.

A high wind does not restrict squirrel activity on the ground as much as it restricts movement in trees. The force of a strong wind against

a squirrel's body and especially against its tail increases the animal's difficulty in maintaining balance while it is in the process of leaping and when it is traversing small branches.

Specific effects of barometric pressure upon squirrel activity are non-evident. Activity is greatest from 30.40 inches to 30.49 inches and from 30.10 inches to 30.29 inches at 800 feet above sea level. Least activity occurs at pressures between 29.60 inches and 29.69 inches.

Intensity of activity is inversely proportional to the degree of cloudiness. Least activity occurs on cloudy days. Greatest activity occurs on clear days. Complete absence of sunshine decreases squirrel activity. Partial sunshine, if only for a brief portion of an observation period, stimulates activity.

Light rains, drizzles and mists are relatively moderate in their effects upon squirrel activity. Snowfall decreases activity but to a lesser extent than does rain. The fox squirrel is more active at those times which have no precipitation than at those which have rain or snow. The effect of fallen snow upon squirrel activity depends upon depth of the snow. Activity is unaffected by snow that is two inches or less deep. Snow more than two inches deep impedes activity. Snow patches have no appreciable effect upon activity.

The effects of each environmental factor must be interpreted only after due consideration has been given to the interrelationships of that specific factor with the other influences comprising the environment.

# BIOLOGY AND CONTROL OF THE TUBER FLEA BEETLE, *EPITRIX TUBERIS* GENTNER, IN NEBRASKA<sup>1</sup>

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The tuber flea beetle, *Epitrix tuberis* Gentner, is the most important of the insect pests found on potatoes in western Nebraska, especially in the irrigated sections of the North Platte Valley. This species, which until recently was considered the same as the potato flea beetle, *E. cucumeris* (Harris), is western in distribution, apparently reaching the eastern limits of its range in Nebraska. Tuber blemishes caused by the feeding activities of the larvae are major factors in lowering the quality of the potato crop.

Tuber flea beetles overwinter in the soil in the adult stage, relatively high average winter survivals being recorded in cage studies. Following spring emergence the adults feed on the foliage of a wide range of plants; 28 different species were recorded as adult hosts. Whenever potatoes were available, they were preferred.

Insectary studies indicated an average preoviposition period of between five and six days; an oviposition period of from 35 to 57 days, averaging 44.7 days; and the number of eggs laid per female ranged from 161 to 215, averaging 187. Eggs usually were deposited in batches of from 12 to 15 with intervals of from 1 to 2 days elapsing between successive depositions.

The average duration of the egg stage ranged from 5.5 to 6.2 days, the larval period from 17.7 to 22.8 days and the average length of the pupal stage varied from 5.8 to 11.2 days. Theoretical total developmental periods of from 27 to 85 days were indicated from this study.

In the Scottsbluff area adults begin emerging from the soil about mid-May and continue to appear until late June or early July. The peak of emergence normally is reached shortly before mid-June. Soon thereafter overwintered beetles move into early planted potato fields. Eggs are laid in the soil around the base of the plants from late May until at least the latter part of July. About July 1, first generation adults begin appearing and attain greatest numbers in early fields during the latter half of July or in early August. During July and early August, when the early crop matures or is harvested, the beetles migrate to nearby late plantings. Here eggs are laid and from these develop the second generation larvae which largely are responsible for tuber injury to the late crop. The first adults of the second generation usually appear about August 10 and reach a peak of abundance sometime between late August and mid-September. In the North Platte Valley two fairly complete generations develop each

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<sup>1</sup> Doctoral thesis No. 818, submitted December 4, 1946.

year, and under some conditions evidence of a partial third has been obtained.

Larval feeding is confined to the underground portions of the plant. "Worm tracks," "pimples" and "slivers" are caused by the larvae feeding on tubers of the potato plant. In Nebraska these blemishes, resulting in low quality potatoes, are far more serious than foliage injury by the adults. Larvae were found to develop on seven different host plants.

Factors of most importance in influencing the abundance of tuber flea beetles are weather conditions, especially rainfall, irrigation, host plants, date of planting the potato crop and the presence or absence of cull dumps.

From data presented it is evident that seasons with above normal rainfall are most favorable for flea beetle development and subsequent tuber injury. Adequate moisture during September and October and the following May and June favors winter survival and spring emergence of the overwintered adults. A comparison of tubers from plots of potatoes receiving five or six irrigations during the season showed almost three times as many larval blemishes as potatoes irrigated twice and nearly eight times the number found on tubers from plots watered once.

The type of food plant consumed by adult flea beetles markedly influenced oviposition and length of life. Potato foliage was the most satisfactory of the nine host plants studied, egg production being highest and mortality lowest on such a diet. The substitution of potato foliage for less nutritious diets was followed in two or three days by increased egg production. A change from potato to foliage of other food plants resulted in decreased egg production. In one 60-day test significant fluctuations in egg deposition were recorded when, at 10-day intervals, diets of potato foliage were alternated with either marsh elder, *Iva xanthifolia*, or buffalo bur, *Solanum rostratum*.

In the field, larvae developed most readily and in largest numbers on potato roots and tubers. Considerably less development occurred on roots of tomato. Relatively few individuals matured on ground cherry, *Physalis lanceolata*, black nightshade, *Solanum nigrum*, buffalo bur and field bean, *Phaseolus vulgaris*. No larval development was recorded from wild tomato, *S. triflorum*, marsh elder or kochia, *Kochia scoparia*.

As a result of these findings and since largest populations of tuber flea beetles were found to occur in localities where early planted potatoes are grown, the elimination of the relatively few such plantings was proposed. The data indicated that the elimination of early plantings would lower the general flea beetle population level by reducing the reproductive capacity and longevity of the overwintered beetles. Without potatoes the overwintered insects would be forced to feed, live and reproduce on less nutritious host plants, thus greatly decreasing the number of first generation beetles available to infest late planted potato fields.

Not only do the larvae reduce the quality of the potato crop but data are presented to show that they also are responsible for a portion of the low total yields often obtained in early planted fields. Approximately

30 per cent of the stolons, or potential tuber-forming parts, were destroyed by the feeding activities of the larvae.

In a varietal susceptibility test involving eight Nebraska adapted varieties, the Bliss Triumph, most widely grown potato in western Nebraska, proved most resistant to larval injury.

Dusts, properly applied, equalled sprays in effectiveness for the control of tuber flea beetles. Of the dusts tested in the earlier experiments (1940-1943), barium fluosilicate and cryolite, which were equally effective, ranked first. Among the sprays used in these early experiments, zinc arsenite and basic copper arsenate proved best. In the 1944 field and insectary experiments, DDT in both spray and dust form was significantly superior to all other materials for controlling flea beetles. DDT-sulfur dusts appeared slightly more efficient than DDT-pyrophyllite mixtures in 1945 tests. To effectively control flea beetles in infested late planted fields three or more treatments were needed. Single applications proved unsatisfactory. Applications made in August or just before the vines closed the rows were of greatest value in the control program.

In a preliminary test, soil applications of DDT-pyrophyllite dusts significantly reduced the amount of larval injury to tubers.

No increases in aphids or other harmful species have occurred following the use of DDT on potatoes in western Nebraska. Although some beneficial insect species were killed with the DDT insecticides, large scale tests indicated that this would have no appreciable effect on the insect problem as a whole.

The cultural practices found effective as control measures for tuber flea beetles also aid in the control of most other pests of the potato in Nebraska.

# WATER CONTENT CHANGES OF POULTRY HELD IN FROZEN STORAGE AS RELATED TO PALATABILITY<sup>1</sup>

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The purpose of this investigation was to explore the nature of water content changes of poultry held in frozen storage and to study the relationship of these changes to juiciness scores.

Vapor pressure analyses for bound water and total water content were made on the pectoralis major breast muscles of 60 roasters. These analyses were made first on the fresh raw muscle, later after frozen storage, and finally after cooking.

The roasters were divided for frozen storage into series A, B, and C, each series containing 20 birds. Each series was then subdivided into two groups, one group of 10 birds being stored at  $-12.2^{\circ}\text{C}$ . ( $10^{\circ}\text{F}$ .) and the other 10 birds being stored at  $-23.3^{\circ}\text{C}$ . ( $-10^{\circ}\text{F}$ .). Series A was stored for 9 months, series B for 6 months, and series C for 9 months. However, series C differed from series A in that samples for vapor pressure analyses were removed from the roasters at the end of 6 months of storage as well as at the end of the 9-month period.

The experimental apparatus used was an isotenoscope type of instrument. Duplicates of samples of the breast muscle were dehydrated at  $27.5^{\circ}\text{C}$ . ( $81.5^{\circ}\text{F}$ .) under a high vacuum. Vapor pressure desorption isotherms were determined for each group of 10 birds in each series (A, B, and C). These isotherms were further analyzed statistically in order to determine absolute differences between them. Only the upper 60 per cent of the R. V. P. range was considered in the comparison analysis.

The vapor pressure method of analysis successfully indicated an increase in bound water in chicken breast muscle during storage and also a further increase in waterbinding capacity as a result of cooking. The longer storage time (9 months) and the higher storage temperature ( $-12.2^{\circ}\text{C}$ .) apparently caused the greater amount of bound water.

The average water content of all of the fresh samples was found to be 74.4 per cent. The free water lost because of storage was slight, but that lost because of cooking was 4.1 per cent.

No correlation was found between juiciness and either bound water or total per cent water in the breast muscle of the roasters. However, further study with an improved palatability scoring plan and a different experimental plan might indicate otherwise. It may be noted, however, that slight correlation trends between bound water and palatability and between total moisture content and palatability did appear in the results.

<sup>1</sup> Doctoral thesis No. 804, submitted July 20, 1946.

Worthy of note is the fact that the vapor pressure of water, as indicated by the experimental apparatus used, varied according to room temperature. It was, therefore, necessary to make corrections experimentally for the vapor pressure readings of the roaster breast muscles.

Equilibrium in the vapor pressure apparatus when making tests was at times difficult to obtain. This was usually true of the cooked samples and occasionally it was true with the uncooked samples. Cooking seemed to complicate the dehydration process and the establishment of vapor pressure equilibrium.

This work seemed to give evidence that in poultry breast muscle protein denaturation continues during frozen storage, being more for the longer storage time, and also for the higher storage temperature. It also offers some experimental evidence that muscle myosin changes from an elongated-shaped molecule to a more rolled-up type of molecule during the denaturation process.



# THE GRADUATED LAND TAX<sup>1</sup>

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The graduated land tax is a progressive tax on land, that is, a tax whose rate increases as the size of the tax base, above specified exemptions, also increases. It may be levied either as a supplemental source of fiscal revenue or as a means of exercising social control over the ownership of land. It is with this latter alternative that this study is concerned.

The specific function of the graduated land tax is to preserve for individuals the opportunity of acquiring land through a limitation on the land which may be owned by any one person. Such a regulatory tax clearly involves the use of the Police Power. The determinants lie in the fields of ethics and politics as well as in economics. Given a condition where access to property is prohibited or impeded by "excessive" land holdings, this study has favored the limitation in the interest of the general welfare. It has also been argued that the limitation would probably be upheld as a valid exercise of the Police Power.

This is the ethico-political foundation of the graduated land tax. The politico-economic problem of the tax is not a matter of principle, but a problem in the *application* of the Police Power. It is in the application of any principle that the method of trial and error, study, and, above all, flexibility to meet the dynamic character of the problem, should prevail. There is no final answer in the application of principle, but in this case, the application of the graduated land tax should be dependent on the evidence of sufficient cause.

The First Legislature of the State of Oklahoma adopted a graduated land tax law in 1908. The law was held unconstitutional by the Oklahoma Supreme Court on the grounds that the Act failed to specify the purpose and disposition of the tax revenue. A second graduated land tax was adopted by the Oklahoma Legislature in 1913. This law has been inferred unconstitutional because of the Oklahoma Supreme Court's ruling on the general revenue section of the Act of which it was a part. The most recent Oklahoma proposal for a graduated land tax came with Initiative Petition No. 145, which was circulated in 1935 and was voted on as a State Question in the general election of 1940. This State Question, although receiving a two to one affirmative margin of the 600,000 votes cast, was rejected because of a constitutional requirement that a State Question must carry a majority in terms of the largest vote on any office in the election. In effect, the silent voters on the Question killed it. The unusual feature of the Oklahoma experience with graduated land tax legislation and pro-

<sup>1</sup> Doctoral thesis No. 854, submitted June 9, 1947.

posals is that, in no instance, has the fundamental principle—that of progressive land taxation—been judicially considered.

Using the existing data relating to the ownership of land in Oklahoma, the provisions of the constitutional amendment proposed in Initiative Petition No. 145 were analyzed. This proposal dealt with land holdings exceeding 640 acres. It was established that in 1935, 2.4 per cent of the State's land owners owned more than 640 acres of land and these holdings amounted to 20.2 per cent of the State's land area. The bulk of these holdings were in the timber land and the grazing land areas of the State.

An initial exemption of \$12,000 assessed value eliminated 49 per cent of the above land holdings. Exemption of timber land and grazing land eliminated another 36 per cent of the large land holdings. Exemption of land acquired by corporations through mortgage foreclosure eliminated another 8 per cent of the land originally classified. There remained subject to the tax but 7 per cent of the original large land holdings embracing roughly 1.5 per cent of the State's land area.

Within the holdings subject to the tax, the excess acreage above the proposed legal maximum amounted to nearly 244,000 acres, or roughly 0.54 per cent of the State's land area. Of the holdings subject to the tax, 78.5 per cent had less than 640 acres excess and these holdings accounted for 43.7 per cent of the excess acreage. It was further estimated that 70.9 per cent of the taxable holdings were owner-operated and that these holdings accounted for 40.2 per cent of the excess acreage. Where the holding was tenant-operated, disposal of excess acreage would have been economically feasible. In the case of the owner-operator, the decision would have been one of weighing loss in income from reduced operations plus investment income against the amount of the tax.

A suggested law was proposed based upon the analysis of Initiative Petition No. 145 and the experience of foreign graduated land taxes. The proposed law would function under a permissive constitutional amendment. Its tax base was predicated upon assessed valuation. An initial exemption of \$25,000 was proposed with an "in lieu" exemption of 320 acres. On the basis of property classification exemptions were also proposed applying to (1) the land of common carriers and public utilities (2) land acquired through collection of debts: this exemption would be limited to seven years (3) improvements on land up to 20 per cent of the assessed value of such land. The proposed rate schedule was composed of 16 rate classes, graduated at intervals of \$2,000 assessed value. The rates were to be increased by their original amount each year for the first five years, after which time they would remain at the highest rate reached.

This proposed law would be effective in breaking up excessive holdings. It would be, however, a law which would have little effect upon the present Oklahoma land ownership pattern. Essentially, it would be a preventive—not a remedial—law.

On the basis of the present study, it would seem that the pattern of land ownership existing in Oklahoma in 1935 did not represent an owner-

ship concentration which would constitute a serious impediment to the acquisition of land. Evidence indicates that the graduated land tax proposal embodied in the Oklahoma Initiative Petition No. 145 would have had little incidence upon the 1935 land ownership pattern. It would appear that a more efficient graduated land tax law could be framed for Oklahoma in terms of preventing a potential concentration of land ownership rather than in terms of remedying the then existing land ownership concentration. This study reveals the need for careful study and analysis preceding the enactment of any graduated land tax legislation. The ends of social justice and economic efficiency require that any such legislation represent a maximum flexibility in terms of the dynamic problem that the graduated land tax seeks to solve.

# EVALUATION OF CERTAIN INSECTICIDES AND DRUGS AS CHEMOTHERAPEUTIC AGENTS FOR EXTERNAL BLOOD SUCKING PARASITES<sup>1</sup>

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In 1944 Lindquist, Knippling, Jones, and Madden (J. Econ. Ent. 37 (1): 128) demonstrated that bedbugs (*Cimex lectularius* L. and *C. hemipterus* F.) were killed when they engorged on rabbits which had been given, orally, high dosages (300 to 500 mg. per kg.) of DDT or pyrethrins. This was the first demonstration that blood sucking arthropods could be destroyed with chemotherapeutic agents.

More extensive investigations in the field of chemotherapy for insect control were undertaken by the writer in 1946, at the Orlando, Florida, laboratory of the Bureau of Entomology and Plant Quarantine. More than 30 selected insecticides and drugs were evaluated when administered to rabbits. These included well-known materials such as pyrethrins, DDT, rotenone, chlorinated camphene (Hercules 3956), chlordane (Velsicol 1068), several indandione derivatives, phenothiazine, the gamma isomer of benzene hexachloride, atabrine, and neoarsphenamine. The value of the chemicals as therapeutic agents was determined by permitting body lice (*Pediculus humanus corporis* Deg.) and mosquitoes (*Aedes aegypti* L.) to engorge on the treated animals. The effect of several materials was determined also for the ear mite *Psoroptes equi* var. *cuniculi* Del. and the tick *Amblyomma americanum* L.

Initial tests were conducted at the relatively high dosage rate of 300 mg. of the chemical per kg. of body weight of the host. The chemicals, undiluted, were administered in gelatin capsules. A stomach tube was employed when they were administered in oil solution. From 25 to 50 lice, and usually from 15 to 50 mosquitoes, were permitted to engorge 6 hours after administration of the chemical to the host. Tests were made also at 24 and usually at 48 hours after the chemical was given to the rabbits. Thereafter, tests were not made unless the mortality records indicated that the chemical was producing some toxic action to the insects. The engorged insects were held at 85°F. and mortality counts were made after 24 hours.

Of thirty-one chemicals evaluated against mosquitoes, several showed some activity but only one, the gamma isomer of benzene hexachloride,

<sup>1</sup> Doctoral thesis No. 838, submitted March 19, 1947.

<sup>2</sup> The studies herein reported were undertaken by the author while engaged in regular research activities sponsored and financed by the Bureau of Entomology and Plant Quarantine, U. S. Department of Agriculture. Details of the investigations will be published at some future date.

caused complete mortality of the insects at the initial dosage of 300 mg. per kg. of body weight of the host. Subsequent tests employing lower dosage levels showed that complete kill of mosquitoes resulted also at 25 and 100 mg. per kg. Most of the animals were killed by the chemical. However, one receiving 100 mg. per kg. survived, and the mosquitoes engorging each day on this host showed complete kill for 5 days. A dosage of 5 mg. per kg. caused a maximum of 93 per cent kill of engorged mosquitoes and caused no apparent harm to the host.

Thirty-three chemicals were evaluated against the body louse. Several of the materials showed activity but only chemicals among the indandione derivatives caused complete mortality at the initial dosage of 300 mg. per kg. One of these, 2-pivalyl-1,3-indandione, proved especially active and subsequent tests showed that oral dosages as low as 2.5 mg. per kg. caused complete or nearly complete kill of lice permitted one blood meal on the host. A dosage of 1 mg. per kg. caused a maximum mortality ranging from 18 to 30 per cent. The chemical appeared to be equally effective when administered orally, subcutaneously, intramuscularly, and intravenously. Some kill of engorged lice resulted when the chemical was applied in solution to the unbroken skin of rabbits, but results were erratic. Oral dosage levels of 5 to 100 mg. per kg. produced complete kill of lice for periods ranging from 3 to 8 days. In each case, however, partial kill was obtained for several days after the mortality dropped below 100 per cent. The duration of the toxic principle in the blood was not in relation to the dosage employed, and host variation seemed a greater factor than the dosage level, within the range indicated.

When rabbits were given oral dosages as low as 0.25 mg. per kg. each day for several days, either by forced administration or in food, the blood of the host became toxic to the insects in less than a week, and nearly complete kill of lice permitted one blood meal was obtained. Thus, it was established that the toxic agent was eliminated slowly and accumulated in the blood of rabbits as a result of daily consumption of low dosages of the chemical.

Lice allowed repeated blood meals on rabbits receiving the chemical were killed at dosages even lower than 0.25 mg. per kg. One animal was given 0.1 mg. per kg. in food each day for 19 days. The rabbit food, Purina pellets, contained 5 parts per million of the chemical. Lice which were allowed only one blood meal on the host during this period usually showed less than 20 per cent mortality in 24 hours, but they were killed when allowed blood meals two times each day for three consecutive days. These results proved that the toxic agent accumulated in the insect. The toxic principle persisted in the blood for over 30 days after the animal was taken off the treated food, as evidenced by high mortality rate (usually 80 per cent or more) of lice permitted three day feeding schedules on the animal. During the 44th to the 46th day period after the animal was denied further treated food, the toxic principle was no longer apparent in the blood since over 90 per cent of both male and female lice survived three days of feeding.

Female lice were more readily killed than were the males. It was determined, however, that females consumed in relation to the body weight about two and one-half times as much blood as did the males. This, no doubt, explains the difference in rate of mortality of the sexes.

Lice were affected very rapidly when they engorged on rabbits which received from 25 to 300 mg. per kg. of 2-pivalyl-1,3-indandione. They were dead or paralyzed within 15 minutes to 1 hour after feeding. The toxic agent was shown to be present in the blood of the host as early as 2 hours after administering the chemical and apparently the maximum concentration developed during the first 24 hours even though the toxic principle persisted in the blood for a week or more in most animals.

A limited number of tests indicated that ear mites of rabbits were killed by benzene hexachloride administered to the host at the rate of 100 to 300 mg. per kg. Partial kill of the ear mites resulted from a dosage of 50 mg. per kg. Larvae and nymphs of *A. americanum* (L.) were not affected by this chemical at a dosage level of 25 mg. per kg.

Engorging larvae and nymphs of *A. americanum* were killed on rabbits receiving 2-pivalyl-1,3-indandione at a dosage of 25 mg. per kg. but not at 5 mg. per kg. Some kill of mosquitoes resulted at 25 mg. per kg. but even 300 mg. per kg. did not cause complete kill. This chemical apparently did not affect ear mites when given to the infested host at the rate of 300 mg. per kg.

No special studies were conducted to determine the toxicological effects on rabbits receiving the various chemicals tested, although a number of the materials caused death at the dosage of 300 mg. per kg. 2-Pivalyl-1,3-indandione proved fatal to the host when given at this high dosage and 100 mg. per kg. proved fatal in some cases. No apparent harmful effects were noted when administered orally at the rate of 25 mg. per kg. or less. It is recognized, however, that toxic effects to the host may have been produced at the lower dosage levels even though they were not apparent. Animals on treated food, which provided 0.25 and 0.1 mg. per kg. of the chemical each day for 19 days, showed no harmful effects.

It is believed that the favorable results obtained in the exploratory investigation definitely establish the potentialities of employing insecticides as internal treatments for the control of insect and other arthropod parasites of animals. Further studies against various animal parasites seem warranted, especially with the materials which showed activity as chemotherapeutic agents in connection with these studies.

# CAUSE AND POSSIBLE PREVENTION OF THE CRACKING OF THIN CONCRETE WALLS POURED INTEGRALLY WITH ARCH-RIBS AND RIGID FRAMES<sup>1</sup>

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The numerous instances of cracking of thin concrete walls when poured integrally with thick base sections, as exemplified by the spandrel and parapet walls of arches and rigid frame bridges, make expedient the investigation of the cause of these cracks and the setting-forth of means for their control.

When the entire cross-section of the Hartland Bridge is used in making the customary analysis for gravity loads and the usual shrinkage and temperature allowances, it is found that the resulting unit stresses are not the controlling cause of cracking.

Replicas, one-twenty-fourth the size of the Hartland Bridge, show the cause of the cracks to arise within the structure. Even though the stresses produced by the shrinkage of the structure as a unit are eliminated the spandrel walls crack at approximately the quarter-points of the span.

Cracking is believed to be caused by the differential volume change which occurs between the thin wall or stem and the thicker rib or base. Differential volume change is the difference in the free volume changes, i.e., changes in length per unit of length between any two contiguous parts. There are two causes of the differential volume change producing cracking, drying shrinkage and drop in atmospheric temperature. The action of drying shrinkage is shown in the Hartland Bridge replicas.

Tee-sections of plaster-sand mortar and neat plaster are used to illustrate the possibility of producing cracks by differential volume change. One specimen cracked when the drying shrinkage was hastened by oven drying. Another cracked in the stem when a temperature differential was produced by means of refrigeration.

The nature of the stresses for both plain and reinforced concrete tee-sections, as produced by a differential volume change, are determined from the mechanics of differential volume change.

The unit stress in the stem of a plain concrete tee-section, as caused by either drying shrinkage or temperature drop, is

$$s'_1 = \Delta E_c \frac{A_1 A_2}{A_1 + A_2} \left( \frac{1}{A_1} - \frac{hz}{2I} \right)$$

where

$\Delta$  = difference in the free volume change of stem and base when considered separated from each other. For shrinkage,  $\Delta$  = shrinkage of stem

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<sup>1</sup> Doctoral thesis No. 813, submitted August 24, 1946.

minus shrinkage of base. For temperature drop,  $\Delta =$  (average temperature of stem minus average temperature of base)  $\times$  coefficient of thermal expansion of concrete.

$A_1, A_2 =$  area of stem and base, respectively.

$h =$  total height of tee-section.

$z =$  distance from centroidal axis to point of stress, positive if above centroidal axis.

$I =$  moment of inertia of tee-section about centroidal axis.

$E_c =$  modulus of elasticity of concrete.

The unit stress in the stem of a reinforced concrete tee-section subjected to drying shrinkage is

$$s'_1 = \frac{p_1 n \Delta'_{F1}}{p_1 n + 1} E_c + \Delta E_c \frac{A'_1 A'_2}{A'_1 + A'_2} \left( \frac{1}{A'_1} - \frac{\bar{a}z}{I_t} \right)$$

where those terms not previously defined are:

$\Delta'_{F1}, \Delta'_{F2} =$  free volume change of stem and base, respectively, if the steel is not bonded to the concrete.

$$\Delta = \frac{\Delta'_{F1}}{p_1 n + 1} - \frac{\Delta'_{F2}}{p'_2 n + 1} \quad .$$

$p_1, p_2 =$  steel ratio for stem and base, respectively.

$A'_1, A'_2 =$  transformed area of stem and base, respectively.

$\bar{a} =$  distance between the centroids of  $A'_1$  and  $A'_2$ .

$$n = \text{the ratio} \frac{E_{\text{steel}}}{E_{\text{concrete}}} = \frac{E_s}{E_c}.$$

$I_t =$  moment of inertia of transformed section.

The unit stress in the stem of a reinforced tee-section subjected to a drop in atmospheric temperature is

$$s'_1 = - \frac{p_1 n (\lambda_s - \lambda_c)}{p_1 n + 1} E_c + \Delta E_c \frac{A'_1 A'_2}{A'_1 + A'_2} \left( \frac{1}{A'_1} - \frac{\bar{a}z}{I_t} \right)$$

where those terms not previously defined are

$\lambda_s, \lambda_c =$  thermal coefficients of expansion of steel and concrete, respectively.

$T_1, T_2 =$  the change in average temperature of stem and base, respectively.

$$\Delta = \frac{(p_1 n \lambda_s + \lambda_c)}{p_1 n + 1} T_1 - \frac{(p_2 n \lambda_s + \lambda_c)}{p_2 n + 1} T_2$$

These stresses are based on a linear stress-strain relationship. In case the use of a non-linear relationship is desired the basic flexure equation is derived and illustrated in the appendices of the thesis.

The analysis of the plain concrete tee-section shows the maximum



unit stress to occur at the juncture of the stem and base and to be appreciably influenced by those factors which affect the value of  $\Delta$ , notably the width of stem as compared to the thickness of base. The maximum unit stress is approximately  $0.75 \Delta E_c$ , tension.

The steel ratios,  $p_1$  and  $p_2$ , have little influence upon the unit stress in the stem and for all practical purposes the section may be considered to be of plain concrete.

When reasonable values for the differential volume change are assigned to  $\Delta$  the critical unit stress approaches the ultimate tensile strength of concrete under the combined influence of drying shrinkage and atmospheric temperature drop. In general it is the combined effect of these phenomena and not either one alone which tends to cause cracking.

Curves for the shrinkage of different thicknesses of slabs have been prepared using observed shrinkages and the loss of evaporable water. Values of  $\Delta$  are obtained from the recommended ultimate shrinkage and the curves showing the differential shrinkage for various slab thicknesses. The field of drying shrinkage has been critically reviewed and evaluated in the appendices.

Average temperature in the different slabs is determined by Schmidt's graphical method and curves showing  $T_1$ - $T_2$  for different temperature drops are shown. The calculated temperature differentials have been verified by field observations on the Hartland Bridge.

The prevention of cracking lies primarily in the control of the amount of  $\Delta$  resulting from drying shrinkage and in offsetting the effect of shrinkage by construction techniques.

The differential volume change resulting from drying shrinkage may be controlled to a considerable degree by careful choice of cement, mix, and aggregates. The cement should show a low percentage of potential chemical compounds, dicalcium silicate and calcium trialuminate. The mix should be lean and the aggregates non-absorptive and rigid.

The amount of differential volume change resulting from both drying shrinkage and temperature drop may be minimized by making the stem width at least half the base thickness. This step alone will prevent cracking in most instances except where the concrete has disproportionately high shrinkage characteristics.

Certain construction techniques give promise of overcoming the effect of differential volume change caused by either drying shrinkage and/or temperature drop. Among these techniques are the precasting in place, curing and shrinking of the stem and that portion of the base immediately beneath the stem, the employment of pre-stressed steel in the stem, the use of absorptive forms for the stem and the construction of the stem of concrete made from expansive cement.

Stem cracking is the result of differential volume change and cannot be controlled by additional stem steel. The answer lies in the use of selected materials, the selection of stem width at least half the base thickness and possibly in suggested construction techniques.

# LINEAR AND CYCLIC AMYLOOLIGOSACCHARIDES AND THEIR RELATIONSHIP TO THE AMYLOLYTIC ENZYMES<sup>1</sup>

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Studies on the straight chain fraction of starch, amylose, are complicated by the refractory nature of the material and the inability to predict its behavior from that of its structural unit, maltose. The desirability of examining homogeneous intermediate molecular weight amylose homologues as a means of simplifying these studies has led a number of investigators to attempt to prepare these compounds. The methods ordinarily used have employed starch as the starting material and involved tedious alcohol fractionations of the acid or enzyme hydrolysate. This investigation presents a method of preparing amyloheptaose, an amylose homologue containing seven glucose units, from Schardinger's  $\beta$ -dextrin. The action of *macerans*,  $\beta$ - and salivary amylases on amyloheptaose and other selected amylooligosaccharides is also reported.

Amyloheptaose was separated from a  $\beta$ -dextrin acid hydrolysate by alcohol precipitation after first removing the  $\beta$ -dextrin. The specific rotation of the material was  $[\alpha]_D^{20} +175.6 \pm 0.5^\circ$ . (Theor.  $179.6^\circ$ ). The molecular weight determined by the Kline and Acree iodine titration was 1206 (Theor. 1152). The reducing power toward alkaline ferricyanide, analysis of the potassium salt of amyloheptaonic acid and chromatography all indicated that the material was essentially pure heptasaccharide.

Previously proposed mechanisms for the action of  $\beta$ -amylase on amylose chains have been confirmed by the examination of the products of digestion of amyloheptaose, the potassium salt of amyloheptaonic acid, and amylopectin.  $\beta$ -amylase removes maltose units from the non-reducing end of the molecule converting straight chains with an even number of glucose units entirely to maltose and those with an odd number of glucose residues to maltose and one molecule of amylotriose.

The primary products from the reaction of salivary amylase on amyloheptaose and amylopectin are maltose and amylotriose. Some glucose is present apparently as a result of the slow hydrolysis of terminal linkages in amylotriose and higher oligosaccharides. Maltose is apparently not hydrolyzed by the salivary amylase preparations used.

The action of *macerans* amylase on amyloheptaose and on Schardinger's  $\alpha$ - and  $\beta$ -dextrins alone and in the presence of co-substrates was examined. *Macerans* amylase was found to be capable of attacking amyloheptaose with the production of  $\alpha$ -dextrin and glucose, maltose, amylo-

<sup>1</sup> Doctoral thesis No. 840, submitted April 19, 1947.

triose and other oligosaccharides without the production of additional end groups. The enzyme is capable of converting  $\beta$ -dextrin to  $\alpha$ -dextrin in the presence of maltose as a co-substrate. Sucrose and gluconic acid do not function as co-substrates for this conversion while the reactivity of glucose is uncertain.  $\beta$ -dextrin alone is stable toward the enzyme. Under similar conditions  $\alpha$ -dextrin is converted to  $\beta$ -dextrin with glucose, maltose, calcium maltobionate,  $\alpha$ -methylglucoside, sucrose and cellobiose functioning as co-substrates. Some indications were obtained that  $\alpha$ -dextrin itself may be slowly attacked. The production of the Schardinger dextrans from linear chains and the interconversion of these dextrans in the presence of co-substrates is accomplished by *macerans* amylase without hydrolysis and the consequent production of new reducing end groups. The enzyme is synthetic in its action as well as degradative, producing linear chains of sufficient length to give detectable iodine colorations. The mechanism of these reactions can be best understood by postulating that the sole function of *macerans* amylase is to promote the exchange of glucosidic linkages between cyclic and linear structures.

# THE MORDANTING OF CELLULOSE-ACETATE RAYON, NYLON, AND SILK WITH POTASSIUM DICHROMATE<sup>1</sup>

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The mordanting of three textile fibers, cellulose-acetate rayon, nylon, and silk with aqueous potassium dichromate has been studied as to the effects of initial pH, concentration, and volume of mordanting bath, temperature and duration of mordanting, and initial weight of the fiber to be mordanted. Chromium fixed on each fiber has been estimated from the ash of the mordanted fiber corrected for its initial ash and checked by gravimetric determination of chromium.

Fixation of chromium sesquioxide on cellulose-acetate rayon from fifty volumes of aqueous potassium dichromate during one hour at 100°C. has been shown to be an increasing rectilinear function of initial pH of mordanting bath, 2.0000 g. solute per gram of fiber, between pH 1.17 and 1.29 and a decreasing rectilinear function between this maximum,  $4.03 \pm 0.05$  per cent, and  $0.96 \pm 0.01$  per cent  $\text{Cr}_2\text{O}_3$  at pH 1.67. Loss of acetyl between pH 0.95 and 2.27 was less than 3.8 per cent of its original 38.57 per cent. No change in wet strength occurred when cellulose-acetate rayon was mordanted at the threshold of fixation, pH 2.27; its strength increased upon mordanting at greater pH, approximately 10 per cent at pH 6.47, and decreased by half its first value at pH 0.91.

Fixation on nylon at variable pH and constant concentration, 0.5000 g. solute per gram of fiber, was a decreasing rectilinear function of initial pH of mordanting bath between  $10.30 \pm 0.02$  per cent  $\text{Cr}_2\text{O}_3$  at pH 0.93 and  $2.54 \pm 0.03$  per cent at pH 1.70.

Fixation on silk fibroin from a like bath proved to be an increasing rectilinear function of initial pH from 0.93 to 1.15 and a decreasing rectilinear function between this maximum,  $8.59 \pm 0.10$  per cent, and  $1.30 \pm 0.30$  per cent  $\text{Cr}_2\text{O}_3$  at pH 2.30. The silk lost strength upon mordanting at pH 2.32 or less and retained but 17 per cent of its original wet strength after mordanting at pH 1.21.

Fixation, exhaustion, and the distribution coefficient for each fiber were logarithmic functions of equilibrated concentration, decreasing for nylon but passing through a maximum for cellulose-acetate rayon and silk.

For each fiber, and during 48 hours at 40°C. as well as during one hour at 100°C., fixation of  $\text{Cr}_2\text{O}_3$  from fifty volumes of aqueous potassium dichromate at constant initial pH was an increasing logarithmic function of equilibrated concentration,

$$x/m = kc^n.$$

<sup>1</sup> Doctoral thesis No. 807, submitted July 20, 1946.

Exhaustion and distribution coefficients at both temperatures were decreasing logarithmic functions of equilibrium concentration. At 40°C. increase in conditioned weight of each fiber upon mordanting, within experimental error of chromic-acid equivalent of fixed  $\text{Cr}_2\text{O}_3$ , and increased absorption of light by mordanted fiber were increasing logarithmic functions of equilibrium concentration.

Fixation of  $\text{Cr}_2\text{O}_3$  on each fiber during one hour from fifty-volumes of aqueous potassium dichromate (2.0000 g. solute per gram of cellulose-acetate rayon at pH 1.15 or 0.5000 g. solute per gram of silk at pH 1.70) has been shown to be, between 25 and 100°C., an increasing logarithmic function of temperature of mordanting,

$$x/m = kT^n.$$

Exhaustion and distribution coefficient also increased logarithmically with temperature of mordanting.

Fixation of  $\text{Cr}_2\text{O}_3$  on cellulose-acetate rayon from fifty volumes of potassium dichromate, 2.0000 g. solute per gram of fiber at pH 1.29, was an increasing logarithmic function of time of mordanting,

$$x/m = kt^n$$

between one and 211 hours at 40°C. and between fifteen minutes and four hours at 100°C. At 40°C. the slope of the logarithmic graph of fixation decreased after 49 hours; at 100°C. this change in slope came at 45 minutes. Exhaustion and distribution coefficient were increasing logarithmic functions of time of mordanting at both temperatures and their graphs changed slope like that of fixation. The mean velocity coefficients for the second discontinuous isothermals were less than those for the first. The diffusion coefficients for the first discontinuous isothermal at 40°C. increased to a constant value; at 100°C. the diffusion coefficients passed through a maximum. Until equilibrium pH at 40°C. became constant, in 100 hours at pH 2.00, it increased semilogarithmically as equilibrium concentration of potassium dichromate decreased. No greater loss than 11 per cent occurred during the first hundred hours' mordanting of cellulose-acetate rayon at 40°C.

Fixation of  $\text{Cr}_2\text{O}_3$  on nylon from fifty volumes of aqueous potassium dichromate, 0.5000 g. solute per gram of fiber at pH 1.15, was a similar increasing logarithmic function of time of mordanting between one and 100 hours at 40°C. and between fifteen minutes and 1.5 hours at 100°C. Exhaustion and distribution coefficient were increasing logarithmic functions of time of mordanting at both temperatures. The velocity coefficient decreased with time at each temperature. At 40°C. the diffusion coefficient remained constant for 64 hours but at 100°C. it rose rapidly. After 49 hours' mordanting at 40°C. and at an equilibrium pH of 1.43 nylon retained but 6 per cent of its original wet strength. Equilibrium pH increased semilogarithmically as equilibrium concentration decreased.

Fixation of  $\text{Cr}_2\text{O}_3$  on silk fibroin from fifty volumes of aqueous potassium dichromate, 0.5000 g. solute per gram of fiber at pH 1.70, progressed

as an increasing logarithmic function of time of mordanting between one and 229 hours at 40°C. and between fifteen minutes and one hour at 100°C. Exhaustion and the distribution coefficient were increasing logarithmic functions of time of mordanting at each temperature. The velocity coefficient decreased with time. At 40°C. the diffusion coefficient kept constant from four to 169 hours but at 100°C. it continuously increased. Wet strength of silk fibroin upon mordanting 100 hours at 40°C. fell to 39 per cent of its first value while the pH of its mordanting bath rose from 1.70 to 3.40. Computation of energy of activation in calorie/mole from either velocity coefficients or distribution coefficients gave the same values, 13820 for cellulose-acetate rayon, 7655 for nylon, and 9707 for silk.

Fixation of  $\text{Cr}_2\text{O}_3$  on each fiber,

$$x/m = kv^n$$

and the exhaustion of mordanting bath during one hour at boiling have been shown to be decreasing logarithmic functions of initial volume of mordanting bath, 2.0000 g. solute per gram of cellulose-acetate rayon or 0.5000 g. solute per gram of nylon or silk, with initial pH of the shortest bath rising upon dilution. The distribution coefficient, until it became constant, was also a logarithmic function of initial volume, decreasing for cellulose-acetate rayon and nylon but increasing for silk. When cellulose-acetate rayon and nylon were mordanted in another set of mordanting baths, like the first except for constant initial pH, fixation and exhaustion decreased, but not logarithmically, with volume of mordanting bath and distribution coefficient increased to a constant value.

Fixation of  $\text{Cr}_2\text{O}_3$  on each fiber during one hour at 100°C. from a constant volume of aqueous potassium dichromate (2.0000 g. solute per gram of cellulose-acetate rayon, 1.5000 g. solute per gram of nylon, or 0.5000 g. solute per gram of silk fibroin) was a decreasing logarithmic function of initial weight of fiber between one and thirteen grams,

$$x/m = km^n.$$

Exhaustion was an increasing logarithmic function of weight of fiber. For nylon the distribution coefficient was an increasing, but for cellulose-acetate rayon and silk a decreasing, logarithmic function of weight of fiber.

# AMYLOSE COMPLEXES WITH ORGANIC ACIDS AND ALKYL HALIDES<sup>1</sup>

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Appreciable amounts of fatty acids are known to be associated with cereal starches. Although several hypotheses as to the nature of the interaction of the fatty acids with starch and the nature of the forces binding these acids to starch have been proposed, not any seemed entirely satisfactory.

In this work it is shown that fatty acids, dicarboxylic acids and alkyl halides form complexes with amylose, the unbranched component of starch. X-ray diffraction patterns produced by these complexes indicate a crystalline structure similar to that of the complexes which amylose forms with iodine and the alcohols (1, 2). The structure consists of close packed helical amylose chains with the molecules of the complexing agents within the helices. The packing of the amylose is not materially influenced by the complexing agents, indicating that the complexing agents are contained in spaces within the structure of the amylose. Of the two possible positions, the space within the helices and the interstitial space, the former appears to be more likely.

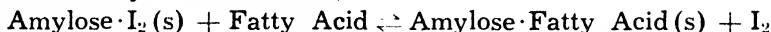
Neither the chain length nor unsaturation of the fatty acid has any effect on the structure of the complex. However, a difference in the X-ray diffraction patterns of the wet and partially dried amylose-fatty acid complexes and of the thoroughly dried complex is noted. The X-ray lines of the latter are definitely shifted to larger angles. In the wet and partially dried samples, the amylose helix has a diameter of 13.7 Å. In the thoroughly dried complex, the helix has a diameter of 13.0 Å, equal to that found for the helix in the amylose-iodine complex (1).

Results are given of a study of the effect of varying amounts of lauric, palmitic, oleic and stearic acids on the iodine binding power of amylose as determined by the potentiometric iodine titration (3). Inhibition of amylose-iodine complex formation is proportional to the fatty acid content of the amylose. This is attributed to a decrease in the capacity of the helices for iodine when the helices contain fatty acids. Evidence is presented that there is a high degree of correlation between the amount of fatty acid bound by helical amylose and the calculated capacity of the interior of the amylose helix. The experimental binding power is from 88 per cent to 91 per cent of the fatty acid calculated on the basis of the helical structure.

Fatty acids can be displaced from the amylose-fatty acid complex by iodine vapors at 70°C. The amounts of fatty acid displaced and the iodine

<sup>1</sup> Doctoral thesis No. 808, submitted July 20, 1946.

gained by the amylose are proportional in the spatial or steric sense. The reversibility of the reaction,



is clearly shown. In aqueous solutions, the equilibrium lies far to the right whereas with dry solids and iodine in the vapor phase, where the iodine activity is greater, the equilibrium is shifted in the opposite direction.

Amylose in the helical "V" configuration binds large amounts of fatty acids when treated with methanol-fatty acid solutions. Retrograded "B" amylose and amylopectin, having essentially the same surface as helical amylose, do not bind significant amounts. This indicates that crystalline configuration is a more important factor than surface in determining whether amylose will bind fatty acids. Adsorption cannot be used satisfactorily to explain the variations mentioned above.

The small amount of fatty acids taken up by amylopectin and the small amount of fatty acids found in the granules of waxy corn starch (which is essentially amylopectin), can be explained very well by the helical hypothesis. Amylopectin, being highly branched, is not capable of forming helices; hence it is not capable of binding the fatty acids.

Amylose in the helical "V" configuration binds an appreciable amount of palmitic acid from a carbon tetrachloride solution low in palmitic acid concentration. Relatively large concentrations of fatty acids are necessary for the introduction of fatty acids into helical amylose from methanol solutions. Methanol is capable of entering the helices of amylose and competing with the fatty acids for space, whereas carbon tetrachloride is not. This also explains the ability of methanol to extract fatty acids from amylose and the inability of carbon tetrachloride to do so. In addition to being able to dissolve fatty acids, a solvent must be capable of displacing the fatty acids from the complexes.

Soaps and other complexing agents will completely precipitate partially dispersed starch. The factors which determine the completeness of precipitation are (1) solubility of the soap and (2) degree of dispersion of the starch granules. Evidence is presented which indicates that in granular starch the amylose and amylopectin are mixed intimately throughout the granules.

Dicarboxylic acids, ethyl adipate and hexamethylene glycol, molecules which have no electric moment parallel to the long axis, form amylose complexes similar to those of iodine, butanol and fatty acids. Hence it is concluded that the dipolar molecules do not seem to be necessary for complex formation with amylose.

Thermal stability of the dicarboxylic acid amylose complexes depend on the chain lengths of the acids. The longer the chain the greater the thermal stability. Partial separation of adipic acid from sebacic acid in mixtures of the two was effected by treating with amylose at 50°C. The greater portion of the sebacic acid precipitated as the amylose complex while most of the adipic acid remained in solution.

Hydrogen bond formation cannot be used to explain the difference



in complexing ability of amylose and amylopectin. Each has essentially the same groups available for bond formation, yet the one forms complexes while the other does not. Neither can hydrogen bond formation be used to explain the interaction between amylose and alkyl halides.

The X-ray diffraction patterns produced by amylose complexes of normal hydrocarbon alkyl halides are identical with those produced by the amylose-butanol and amylose-iodine complexes. The patterns produced by branched alkyl halides are identical with those produced by branched alcohols (4).

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# THE NITROGEN FACTOR IN SWEET POTATO PRODUCTION IN IOWA<sup>1</sup>

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Sweet potato production has been an important enterprise on the sandy soils of southeastern Iowa since 1865. The largest production area of 1,500 acres is located in the Fruitland district of Muscatine County, with smaller acreages located near Conesville, Burlington, Montrose and Carlisle. A sound fertilization program has been an important problem of these growers for many years, and although previous investigations had shown the value of phosphorus and potash, little had been done concerning the role of nitrogen.

The literature relative to the problem indicates that nitrogen applications have increased yields on most sandy soils devoted to sweet potato culture and on some of the heavier textured soils of the south where leaching is an important factor. Shape and the chemical composition of the roots are reported as not being altered by nitrogen applications.

In this study nitrogen fertilizers were tested for their effect on the yield, grade, storage quality and chemical composition of sweet potatoes. The effect of nitrogen on production was studied by means of field tests established on the Muscatine Island Field Station located near Fruitland, with the following general experiments being conducted:

1. A factorial experiment with three levels each of nitrogen, phosphorus and potassium, designed for the purpose of establishing the proper rate and balance of nitrogen when in combination with other nutrients.
2. A time of nitrogen application experiment designed to test the result of early, late and split applications of nitrogen on yield and quality.
3. A nitrogen carrier test outlined to ascertain the most suitable source of nitrogen for the conditions involved.
4. Miscellaneous experiments to compare manure and commercial fertilizers and to test the value of nitrogen in starter solutions.

Sweet potatoes from the various treatments in Experiment 2 were placed in storage in 1938 and 1939 for the purpose of determining the effect of nitrogen on the keeping quality of the roots when applied at different intervals during the growing season. Potatoes from the same treatments were collected and analyzed for sugar, starch and nitrogen content.

At the beginning of the investigation a preliminary survey was made on the nitrate, total nitrogen and organic matter content, and the moisture constants of the soil.

<sup>1</sup> Doctoral thesis No. 641, submitted July 12, 1941.

The field experiments were laid out in approved designs and the data were subjected to appropriate statistical analysis. Fertilizers applied before planting were placed in bands 8 to 10 inches deep in the center of the ridge, while those applied as sidedressings were broadcast by hand along the side of the ridge and cultivated in. Observations were kept on relative foliage color and rate of vine growth; yield records were obtained by recording the weights of No. 1, No. 2 and cull grades and any differences in shape, color, or degree of maturity of the roots were noted.

Rates of applications in Experiment 1 ranged from 22.5 to 75 pounds of nitrogen per acre, 20 to 52.8 pounds of phosphorus and 54 to 108 pounds of potassium. Since nitrogen was the variable in the other experiments, all of the plots received approximately 90 pounds each of  $P_2O_5$  and  $K_2O$  before planting. Except for the check treatments which received none, nitrogen was supplied at the rate of 45 pounds per acre in Experiments 2 and 3. Aside from the check and a treatment receiving all of the nitrogen before planting, the treatments in Experiment 2, where applications were made at monthly intervals, were extended from the time of planting to two months after planting. The nitrogen carriers tested in Experiment 3 were nitrate of soda, ammonium sulfate, Uramon, calcium cyanamid and calcium nitrate.

For the storage tests one bushel, 50 pounds, of No. 1 grade roots was selected from each replication of each treatment of Experiment 2 and stored in bushel baskets in a special room in a local commercial storage house. The following March, the lots were examined for shrinkage and losses due to rots.

For the physiological tests, 30 potatoes were selected at random from each set of treatments in Experiment 2 and, from these, 100 gram samples were killed and stored in 80 per cent alcohol until the analyses for sugars, starch and nitrogen were run. Samples for the 1938 crop were taken from the storage lots in March; but for the 1939 crop, the samples were collected in the fall, cured for 3 weeks, then killed in alcohol.

Both the 1938 and the 1939 seasons had periods of comparatively heavy rainfall and the total for the season was well above average, whereas 1940 was relatively dry throughout, except for a wet week about the middle of August.

The soil in the Fruitland district is classed as a Buckner coarse sand, which is very porous and is underlain with gravel. This soil is very low in total nitrogen, organic matter, base exchange capacity and water holding capacity. The soil is fairly acid, ranging from pH 4.6 to 5.5.

During the three years of this investigation, results in the field tests were obtained as follows:

Experiment 1. Nitrogen applications in two of the three seasons improved the color and growth of the vines, increased yields and produced a higher percentage of U. S. No. 1 grade potatoes. In the dry season, 1940, although vine growth was improved, nitrogen fertilizers either failed to show any beneficial effect on or caused a depression of yields. Amounts between 25 and 45 pounds of nitrogen per acre were adequate in those

years of heavy rainfall, when the applications proved beneficial. Phosphorus and potassium applications proved highly essential in production of sweet potatoes on these soils. The most economical rates were approximately 20 pounds of phosphorus and 75 pounds of potassium per acre.

Experiment 2. The results of these tests indicate that sweet potatoes are rather sensitive to the supply of nitrates in the soil. Yield responses from nitrogen fertilizers were obtained whenever leaching of the natural soil nitrates occurred from spring or early summer rains. Since applications in years of abnormally low rainfall were detrimental in some cases, applications of nitrogen should be made after the character of the season has begun to unfold. In the event of fairly heavy spring rains, an initial application of 25 pounds of nitrogen per acre should be made three to four weeks after planting. With abnormally heavy summer precipitation, a second application midway in the growing season should prove beneficial.

Experiment 3. Nitrate of soda and ammonium sulfate were satisfactory for either preplanting or sidedress application, but as may be expected, the nitrogen in these inorganic forms was subject to leaching. Although calcium cyanamid was very satisfactory in the wet years when applied two weeks prior to planting, it was distinctly injurious in 1940, the dry year. Also the toxic properties of this material make it unsuited for sidedress applications even in years of heavy precipitation.

Experiment 4. Barnyard manures in general were not as satisfactory as commercial fertilizers. Starter solutions used at the time of transplanting gave the plants a faster start, but the effect was of short duration and did not increase the yield.

The results of storage tests showed that applications of nitrogen did not impair the keeping qualities of sweet potatoes, and in the 1939 trial there were fewer rots in the lots from treatments receiving late applications than from the check or the treatment receiving all of the nitrogen before planting.

The sugar and starch content of the sweet potatoes was not altered by the nitrogen treatments, regardless of the time of application. Nitrogen applications materially increased the colloidal nitrogen content of the roots, particularly when applied a month or two after planting.

In summary, nitrogen is an important factor in the production of sweet potatoes in the Fruitland district. Since sweet potatoes are sensitive to an oversupply of nitrates in the soil, applications must be made judiciously, usually at the rate of 25 pounds of nitrogen per acre, applied in an inorganic form and as sidedressings after periods of rather heavy rainfall.

# THE MANUFACTURE OF BLUE CHEESE FROM PASTEURIZED MILK<sup>1</sup>

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Interest in the manufacture of blue cheese from pasteurized milk is increasing rapidly. Pasteurization is desirable for the control of certain microbial defects, such as gasiness and unclean flavors, as well as from the public health standpoint.

A study was made of some possible means by which blue cheese could be made from pasteurized milk and still develop the flavor characteristic of the product made from raw milk. Previous studies have indicated the effect of pasteurization is attributable, to a large degree, to the inactivation of the normal milk lipase, resulting in a decrease in fat degradation in the cheese made from pasteurized milk. Attention therefore was centered upon means for obtaining an increased production of free fatty acids and the ketones derived therefrom in blue cheese made from pasteurized milk.

A total of 143 lots of cheese was made. Seven lots were made with the addition of varying amounts of the lower molecular weight fatty acids. The addition of the acids improved the flavor of the cheese but did not give the flavor typical of good blue cheese.

The addition of cultures of three lipolytic bacteria and one lipolytic yeast to milk for cheese making was tried. Cultures of the organisms grown in cream containing 18 per cent fat were tried in 16 lots of cheese; the same organisms grown in homogenized whole milk were used in 16 lots of cheese. In both series *Mycotorula lipolytica* improved the flavor of the cheese and in some cases caused excessive fat breakdown. *Alcaligenes lipolyticus* gave the cheese unnatural flavors and did not cause appreciable fat degradation. The cheese made with *Achromobacter lipolyticum* and *Pseudomonas fragi* added to the milk were musty and unclean, and showed no evidence of fat hydrolysis by the organisms.

Eleven strains of *Mycotorula lipolytica* isolated from various dairy products at different times were used in 28 lots of cheese to determine the effects of different strains of the organism. Most strains improved the flavor of the cheese, but strains 839, 843, M.L., 848, and 846 gave the most improvement in flavor. These same strains in slightly different order gave the most improvement in flavor in second trials.

A collection of 18 strains of mold of the *Penicillium roqueforti* type was assembled from various sources. These were tested for lipolytic ability by the Nile-blue sulfate technique and for proteolytic ability by Freudenreich's technique on Czapek's agar. Wide variations in lipolytic

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<sup>1</sup> Doctoral thesis No. 849, submitted June 7, 1947.

and proteolytic ability were shown by the different cultures on regular Czapek's agar. The lipolytic ability of the cultures was much greater and about equal for all cultures when the sugar in Czapek's agar was replaced by peptone.

From the results of the tests reported in the preceding paragraph, eight strains were chosen, and a lot of cheese from homogenized raw milk and one from homogenized pasteurized milk were made with each strain. No strain was found to be especially suited to the manufacture of blue cheese from pasteurized milk. Strains 6 and 7 gave the best results in both types of cheese, and strain 17 gave the best result in cheese made from homogenized raw milk.

The addition of an emulsion of a well-cured, fine-flavored cheese to the milk from which blue cheese was made proved very unsuccessful, apparently due to the transfer of contaminating microorganisms, presumably yeasts, to the milk and subsequent development of a yeasty flavor defect in the cheese.

A mold-enzyme preparation was made by the growth of *Penicillium roqueforti* on a modified Czapek's medium which was semi-solid, low in carbohydrate content, and contained 10 per cent butterfat. This was added to the milk at the rate of 0.55 per cent and gave cheese with a very high flavor and excessive rancidity after curing for 12 weeks. Similar preparations were made with five strains of mold of the *Penicillium roqueforti* type and added to milk in amounts varying from 0.05 to 0.25 per cent. All strains brought about an improvement in flavor, although some improved the flavor more than others. The optimum amount of mold-enzyme preparation to use was between 0.10 and 0.25 per cent, depending upon the sharpness of flavor desired. Strains 4, 12, and 6 gave the greatest improvement in flavor, while strain 13 gave the least improvement in flavor.

Protein degradation studies were made on a portion of the trials in an attempt to correlate protein breakdown with flavor development. Little or no correlation of values for amino nitrogen, nitrogen fraction soluble in trichloroacetic acid, and nitrogen fraction soluble in phosphotungstic acid with the flavor scores of the cheese was found.

Fat acidity and total volatile acidity were determined in an attempt to correlate fat degradation with flavor development. Fat acidity showed no apparent relation to the flavor score of blue cheese. The values for total volatile acidity correlated fairly well with the flavor scores. The total volatile acidity was the only chemical determination employed which could be used to predict the flavor score with any degree of precision. Cheese with total volatile acidities in the range in which 30 to 55 ml. of 0.1 *N.* alkali were required to titrate the volatile acids in the first 1000 ml. of steam distillate from 200 g. of cheese, generally had the highest flavor scores.

# THE LIPOLYTIC ENZYME SYSTEM OF *MYCOTORULA LIPOLYTICA*<sup>1</sup>

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Pasteurization of milk is known to destroy milk lipase, which is essential in the normal ripening of blue cheese. This study was undertaken to explore the possibilities of substituting a microbial lipase for the normal milk lipase in the manufacture of blue cheese from pasteurized milk.

Lipase activity was determined by allowing the enzyme to react upon 5 per cent butterfat, emulsified in semi-solid agar, for 48 hours at 37° C., after which the liberated free fatty acids were titrated with N/20 potassium hydroxide in methyl alcohol with phenolphthalein as indicator.

*Mycotorula lipolytica* was selected for a study of its lipolytic enzyme system because this microorganism possessed strong lipolytic and weak oxidative properties and produced considerably more lipase in nutrient broth than either *Achromobacter lipolyticum* or *Pseudomonas fragi*.

Of the five growth media studied in the early phases of the investigation, nutrient broth containing 0.05 per cent glucose was most suitable for lipase production by *M. lipolytica*. Partially-defined synthetic media and skim milk or whole homogenized milk proved much less satisfactory.

Lipase production by *M. lipolytica* took place at pH levels from pH 3.5 to 8.5 with pH 4.5–5.5 as optimum. The addition of 0.225 m disodium phosphate plus citric acid was sufficient to maintain a constant pH level over growth periods of from 4 to 6 days. An equal addition of disodium phosphate plus monopotassium phosphate gave similar results. A sodium acetate plus acetic acid buffer was unsatisfactory. The presence of 0.450 and 0.675 m disodium phosphate plus citric acid was even more favorable for lipase accumulation than was a concentration of 0.225 m at the same reaction of the medium.

Growth of the organism and lipase production took place at temperatures from 21° to 36° C., with 30° C. as optimum for the production of lipase, while highest counts were obtained at 25° C.

The accumulation of lipase in the medium was favored by growing the culture without shaking. Continuous aeration of growing cultures resulted in but little lipase production, while the growth rate of the cells was considerably increased as compared with non-aerated controls.

In general short oval cells and low lipase activity were associated with conditions favorable for rapid growth, while long oval and slender cells and high lipase activity were associated with conditions slightly less favorable for growth.

<sup>1</sup> Doctoral thesis No. 855, submitted June 9, 1947.

Lipase activity on butterfat was demonstrated over a range of reaction from pH 4.0 to pH 8.0, with pH 6.2–6.5 as optimum.

Activity was demonstrated at temperatures from 10° to 52° C. Temperatures of 37° C. and above tended to inactivate the enzyme, the effect being more pronounced with higher temperatures. At 10° C. lipase activity continued at a relatively low but constant rate over a 30-day period.

A storage temperature of 5° C. was much superior to 25° C. for preserving the enzyme in cell-free preparations, activity being maintained at a high level for at least 3 months when storage was at the lower temperature in closed containers.

Lyophilized enzyme preparations retained about half their original total lipase activity and had a high enzyme concentration per unit weight. Considerable concentration of lipase by foaming with carbon dioxide was demonstrated; high losses of enzyme occurred during the process.

Salting-out of lipase with saturated ammonium sulfate plus 30 per cent of 95 per cent ethyl alcohol resulted in a white precipitate high in lipase activity. The activity of this preparation represented only a very small portion of the original lipase activity of the culture. Treatments at 6° C. resulted in more active preparations than treatments at 24° C.

The beneficial effect of cell-free preparations of lipolytic enzyme from *M. lipolytica* upon the ripening of blue cheese made from pasteurized homogenized milk was observed by organoleptic tests as well as by determinations of steam-distillable volatile acid on cheese ripened for 4 and 12 weeks. This enzyme was considered of potential value in the production of blue cheese from pasteurized milk on a commercial scale.



# EVALUATION OF AMYLOLYTIC AGENTS EMPLOYED IN THE ALCOHOLIC FERMENTATION<sup>1</sup>

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Chemical tests previously devised for determining the enzymic activity of amylolytic agents include polarimetric, iodometric, reducing power, and viscosity measurements. In general these chemical tests measure the  $\alpha$ -amylase,  $\beta$ -amylase, or the total  $\alpha$ - and  $\beta$ -amylase activity of the agent employed, and, although they afford rapid measures of the potencies, there can be found no correlation between any of these test methods and actual performance in saccharifying fermentation mashes, particularly with the fungal amylase products known as mold brans. This investigation was initiated because of the lack of correlation of the chemical tests and the need for a test for fungal amylase products prepared with strains of *Aspergillus oryzae* that would have all the advantages and merits of the most conclusive evaluation method, namely, the tedious three to four day conventional fermentation, but would require a shorter period of time and give an exact fermentative evaluation.

Graphical and mathematical analysis of meager fermentation data covering only limited levels of mold bran and ethanol yields from the conventional 72-hour corn mash fermentations indicated a straight line function. This straight line function was obtained by plotting

$\frac{\text{weight of mold bran}}{\text{weight of ethanol}}$  against the weight of mold bran. Based upon this

graphical and mathematical principle a rapid and simple 24-hour fermentation test procedure was developed, which was designated as the "Standard Evaluation Test."

After extended investigations of corn mashes and food grade corn starch media of three starch concentrations, the test medium adopted as most satisfactory for the Standard Evaluation Test contained 100.0 g. of corn starch and 5.0 g. of Difco yeast extract in each wide-mouthed 1-liter Erlenmeyer flask. These ingredients were mixed with 250 ml. of 0.05 normal hydrochloric acid, the starch gelatinized by heating in a water bath with continuous stirring, and the mashes cooked for 60 minutes at 20 pounds steam pressure. To the hot mash in each flask were added concentrated sodium carbonate solution to adjust the pH between 5.0 and 5.3 and the amylolytic agent under test as a slurry in 250 ml. of cold water of such temperature that the resultant mash temperature, after mixing for one minute with a high speed mixer, was about 55° C. Four

<sup>1</sup> Doctoral thesis No. 852, submitted June 9, 1947.

levels of 1.0 g., 2.0 g., 3.0 g., and 4.0 g. of mold bran were used in triplicate in each series. The mashes were cooled to 30° C., inoculated with 20 ml. of a 24-hour yeast culture and incubated at 30° C. for 24 hours, after which the alcohol content for each flask was determined by distillation and subsequent specific gravity measurement. The data were plotted as

$\frac{\text{weight of mold bran}}{\text{weight of ethanol}}$  against weight of mold bran. When the curves

were extrapolated to the Y-axis parallel straight lines having different numerical intercepts were obtained, the intercepts being inversely proportional to the relative amylolytic activity of the various agents employed. This relationship held for the 17 samples, of widely differing amylolytic activity, including laboratory, pilot plant, semi-commercial, plant experimental, and commercial samples, which were tested and evaluated. The intercepts obtained from the curves are shown in Table 1.

SUMMARIZED DATA OBTAINED WITH THE STANDARD EVALUATION TEST PROCEDURE

Mold Bran	Type	Graphical Intercept Value	Minimum Optimal Levels for Maximum Ethanol Production	
			Calculated	Experimental
FCPC No. 1	Laboratory	0 0100	2 00	2.5
MB No. 9	Commercial	0 0131	2.62	2.6
SLI	Commercial	0 0132	2.64	2.6
FCPC No. 2	Semi-commer.	0 0133	(2.66)*	2.66
JWC	Commercial	0 0144	2.88	3.0
UN	Pilot plant	0 0156	3.12	3.5
MB No. 2	Concentrate	0 0163	3.26	
MB No. 4	Plant exper.	0 0177	3.54	
MB No. 1	Commercial	0 0200	4.00	4.0
MB No. 10	Commercial	0 0210	4.20	4.2
MB No. 11	Commercial	0.0213	4.26	4.3
MB No. 5	Plant exper.	0 0236	4.72	
ISC No. 2	Laboratory	0 0240	4.80	4.8
MB No. 6	Plant exper.	0 0250	5.00	
ISC No. 1	Laboratory	0 0264	5.28	5.3
MB No. 3	Plant exper.	0 0303	6.06	
MB No. 12	Commercial	0.0378	7.56	7.6

\* Determined experimentally.

Since the slopes from all the test curves obtained in the Standard Evaluation Tests had practically the same value of about 0.0274, an alternate procedure was found possible employing a single level of 3.0 g. of mold bran per flask instead of four levels. The intercept was then calculated from the straight line equation,  $y = mx + b$ . Although probably not quite as accurate as the Standard Evaluation Test using four levels of amylolytic agent, this one-level method was sufficiently accurate for commercial laboratory control work.

Using the Standard Evaluation Test procedure an exact fermentation evaluation was thus possible, since as the values of the intercepts vary between two agents, the minimum optimal levels for maximum ethanol production vary in the same ratio. Correlation of the intercept values from the Standard Evaluation Tests with the minimum optimal requirements for maximum ethanol production was made by first carrying out conventional 72-hour corn fermentations with various levels of a standard reference sample to ascertain the minimum optimal level of this sample for maximum ethanol yields. Then the proportion

$$\frac{\text{intercept (standard agent)}}{\text{intercept (unknown agent)}} = \frac{\text{optimum level (standard agent)}}{\text{optimum level (unknown agent)}}$$

was employed to compute the minimum optimal level for maximum ethanol production for the other amyolytic agents evaluated. The calculated values are shown in Table 1. Finally to confirm the computed minimum optimal level of each agent actual maximum ethanol production data were obtained for most samples from conventional 72-hour corn fermentations employing six different levels of each amyolytic agent, over a range which included the computed minimum optimal level. The optimum levels thus determined experimentally are also shown in Table 1. The computed and experimentally determined minimum optimal levels for most of the samples gave excellent agreement.

The rapid evaluation of fungal amyolytic agents as to their relative activities and also as to their minimum optimal requirements for maximum ethanol production is thus possible. Any good agent is selected as a reference standard, and the intercept and numerical value for the slope obtained for this reference material by the Standard Evaluation Test. Conventional 72-hour grain fermentations are then carried out employing various levels of the same reference agent to determine the minimum optimal requirement for maximum ethanol production. To evaluate any other agent the intercept is obtained, either graphically by plotting data from the regular Standard Evaluation Test employing four levels of agent, or calculated from the straight line equation employing single-level data. From the intercept the minimum optimal requirement is then computed from the proportion:

$$\frac{\text{intercept (standard agent)}}{\text{intercept (unknown agent)}} = \frac{\text{optimum level (standard agent)}}{\text{optimum level (unknown agent)}}$$

# THE LIFE HISTORY AND MANAGEMENT OF THE WHITE BASS, *LEPIBEMA CHRYSOPS* (RAFINESQUE), IN SPIRIT LAKE, IOWA<sup>1</sup>

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While the natural range of the white bass (*Lepibema chrysops*) presumably does not extend west of the Mississippi River drainage, the largest concentration of this fish in Iowa is in the Okoboji Lake chain, a branch of the Missouri River system. According to records in the Iowa State Conservation Commission files, 100,000 white bass were stocked in the Okoboji Lake chain in 1898. Whether or not there were white bass in Spirit Lake before this stocking is not known, but it appears improbable. White bass have been taken from the lake as long as some of the older residents can remember, and the population has ranged from one of the most abundant fish in the lake to near extinction. Since 1939 it has appeared prominently in the catch, and has presumably been of considerable influence in the ecology of the lake.

The study of the Spirit Lake white bass was started in 1942, and the field work was completed in 1946. In addition to the material collected by the writer, information on 22 white bass was used from the 1941 collections of Max Davis<sup>2</sup> and Tom Moen. Dr. R. M. Bailey collected 31 specimens for the project between April and July, 1943. No collections were made in 1944. The study of the Spirit Lake white bass was based on fish taken in 1941, 1942, 1943, 1945, and 1946. The data were obtained from the following number of specimens: Body-scale ratio, 1,142; length-weight relationship, 1,459; analyses of stomach contents, 972.

The collection of the young-of-the-year Spirit Lake white bass was made largely with a 400-foot seine equipped with a ½ inch stretched-measure bag and with ¾ inch stretched-measure wings. The white bass, other than the young fish, were taken by hook and line, by means of gill-nets, and with seines ranging in length from 25 feet to 2,000 feet. The two types of gill-nets used during the investigation were commercial nets similar to those commonly used by the local fishermen, and experimental nets.

Spirit Lake is a shallow, rich, hard water, eutrophic lake not exceeding 23 feet in depth, except during short intervals. Spirit Lake and its watershed are covered by Wisconsin glacial drift. The normal temperature for the Northwest Iowa District is 46.6 degrees Fahrenheit, the normal precipitation is 28.40 inches, and the normal growing season is 148 days. *Potamogeton richardsonii* and *Scirpus acutus* are the dominant

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<sup>1</sup> Doctoral thesis No. 846, submitted June 6, 1947.

<sup>2</sup> Killed in action, 1944.

deep-water plants. The fluctuations in the water level elevations in the last 13 years apparently have not exceeded nine feet. A combination of silting and decomposition of organic material has leveled the lake bed and decreased the average depth in the last 30 years. Siltation of the lake, as a result of agricultural activities, probably is a minor factor.

An estimate of the relative abundance of the more common Spirit Lake fish was made by evaluative information from rough-fish removal operations, gill-netting catches, test-seining results, hook and line fishing, and a dead fish survey. In general, the young of the pan and game fish amounted to a very large percentage of all of the small fish in the lake. The young of yellow perch (*Perca flavescens*), black crappie (*Pomoxis nigro-maculatus*), common bluegill (*Lepomis macrochirus macrochirus*), and northern black bullhead (*Ameiurus melas melas*) accounted for almost all of the small pan fish. Young-of-the-year white bass were quite common in 1942; young largemouth bass (*Huro salmoides*) were somewhat less common in 1945 and 1946. The number of small pan fish was always many times greater than that of the young game fish. Adults of yellow perch and black bullhead were very abundant for every year considered. The carp (*Cyprinus carpio*) was the most common non-game food fish. The two species of gar, the shortnose (*Lepisosteus platostomus*) and the northern longnose (*Lepisosteus osseus oxyurus*), were not common. Etheostominae were more numerous than native Cyprinidae, but neither were common. The walleye (*Stizostedion vitreum vitreum*), and the northern pike (*Esox lucius*), were the most common of the larger game fish.

The average spawning date for white bass in 1946 was believed to have been sometime during the last week in May. The water temperature for this period was approximately 60 degrees Fahrenheit. Attempts to obtain and fertilize eggs for incubation in the fish hatchery met with uniform failure. Mature fish in two small ponds apparently did not reproduce successfully.

The body-scale relationship can be described as a regression line having a Y intercept (length axis) of 23.89 and a slope of 1.883. The females grew faster and larger than the males, but they did not live as long. The 1941 year-class dominated the population from 1942 through 1946. The average growing season is estimated to be between 125 and 150 days. The most rapid growths occur in June, July, and August. The average date of annulus completion for the 1941 year-class in 1945 was early in August. There was virtually no growth of the 1941 year-class in 1946. While none of the fish was mature at the end of their first year, apparently all, or almost all, were adult at the end of three years. A larger number of females than males were mature at the end of the second year of life. The mathematical relationship between the length and weight, for all data combined, may be expressed by the equation:

$$W = 9.688 \times 10^{-4} L^{3.206}$$

The coefficient of condition increased irregularly as the length increased regardless of sex or age.

The Spirit Lake white bass fed almost entirely on fish, insects, and crustaceans. The bluegill and the black crappie composed the bulk of the fish food. Game fish were an unimportant item. Non-game food fish, excluding the freshwater sheepshead (*Aplodinotus grunniens*), were not taken. The two orders of insects taken most often were Diptera and Ephemeroptera. *Leptodora kindti* was the most frequently determined crustacean. The larger white bass tended to feed more on fish, while the young fed largely on invertebrates. There was little or no feeding activity under the ice. With the advent of warm weather the white bass remained in deep water during the day, and moved inshore at twilight.

Abundant year-classes of white bass should be harvested rapidly with little or no restriction on either the size or the number taken. During periods of low populations the season should remain closed on immature fish and adult fish that have not spawned during the current year. Fish just reaching maturity rather than adults nearing senility should be used for stocking purposes. Careful consideration should be given to the possible effects on more desirable game fish before white bass are introduced into a lake or stream.

# SOME FACTORS AFFECTING THE FUNCTIONAL PROPERTIES OF LIQUID EGG ALBUMEN<sup>1</sup>

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A study has been made of some factors affecting the beating and leavening properties of egg albumen.

A whip test, which fairly accurately measures the property of egg albumen to perform in angel cake was devised and used. This test was an accurate measure of changes in egg white resulting from certain treatments such as heating, acidification, fermentation and homogenization. The test was capable of showing slight differences in treatment and correlated fairly closely with actual performance of the white in angel cake. However, many factors affect the relationship between the whipping test and the angel cake performance. Good correlation holds only under certain specified and tested conditions to certain limitations. It is necessary to determine the correlation of the whip test and angel cake performance with each specific treatment so that erroneous conclusions will not be drawn.

It was found that fresh egg white loses its foaming property when heated to 142° F. Holding periods in excess of 30 seconds at 140° F. resulted in a loss in angel cake performance. Holding times at a temperature of 120° F. for one hour or more resulted in similar losses in beating and cake performance.

Lowering the pH of egg white from 8.5 to 7.0-6.0 by acid results in a slight loss of beating capacity. However, the stability to heat is definitely increased by such adjustments. Fermentation also lowers the pH of egg white but the loss of beating power in this case is not observed until a pH of 6.6 or lower is reached.

The addition of sugars to egg white resulted in a definite beneficial effect on its functional properties when subjected to various treatments. Sucrose exhibited a marked heat stabilizing effect on egg white. The stabilization to heat increased with increase in sugar concentration.

It was also shown that at the same concentrations, glucose, lactose and maltose were more effective in stabilizing the egg white to heat than were sucrose and mannitol. Glycerol exhibited the same effect as did sucrose. Ethylene glycol, triethylene glycol and polyethylene glycol, although increasing the beating power of egg white prior to heat treatment had an adverse effect on heating. The loss of whipping property was greater on heating when these glycols were added than when the egg white was heated alone.

The addition of sugars to egg white increased the whipping power.

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<sup>1</sup> Doctoral thesis No. 823, submitted December 13, 1946.

Sugar also permitted the pH of egg white to be lowered to 6.5 without impairing the initial foaming capacity.

The addition of sodium chloride in concentrations up to 1.0 per cent had no effect on the initial foaming rate of egg white. When subjected to heat, however, these low concentrations did show a slight stabilizing effect.

It is suggested that the results of this study indicate that mucin plays an important role in the whipping property and angel cake performance of egg white. Adjusting the pH to near the isoelectric point of mucin results in a loss in cake performance. In addition when thick white (containing a majority of mucin) is heated a greater loss in whipping property occurred than when heating thin white.

Homogenization resulted in a definite loss of whipping capacity; this effect varied with the homogenization pressure used. The addition of sugar and lowering the pH did not have any beneficial effect when homogenization was used. Angel cake performance did not always correlate with the beating test. For instance, satisfactory cakes were made from egg whites homogenized at low pressures. However, when high homogenizing pressures were used unsatisfactory cake performance resulted.



# THE SYNTHESIS, RESOLUTION, AND METABOLISM OF TYROSINE ISOMERS AND ANALOGUES<sup>1</sup>

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Earlier studies have shown that vitamin C is essential for the complete metabolism of phenylalanine and tyrosine. It has also been established that the alteration of the structure of these amino acids through the formation of simple derivatives, causes these compounds to be no longer dependent upon an adequate supply of the vitamin for their complete metabolism. To further study the interrelation between vitamin C and the metabolism of these aromatic amino acids, the various isomers and analogues were needed in optically active form. This investigation studied the synthesis and resolution of *ortho*-tyrosine, *meta*-tyrosine, 2,5-dihydroxyphenylalanine, 2,4-dihydroxyphenylalanine, and 2,3-dihydroxyphenylalanine. Also, preliminary metabolic investigation of *l* and *d* isomers of *meta*-tyrosine was undertaken using the Warburg manometric technique.

*meta*-Tyrosine was synthesized by a modified Erlenmeyer method which involved the reaction of hydriodic acid with the azlactone formed through the condensation of acetylglycine and *m*-hydroxybenzaldehyde. The N-formyl derivative of this amino acid formed a brucine salt one diastereoisomer of which was alcohol soluble but water insoluble. As the other diastereoisomer exhibited the inverse solubility relationships, separation of the optically active forms through repeated recrystallization was possible.

The application of the isomers of *meta*-tyrosine to metabolic study required the establishment of configuration of the *d*- and *l*-enantiomorphs isolated. This was accomplished by two methods. In the first, the procedure of Lutz and Jirgensons<sup>2</sup> was made use of which involved the measurement of optical activity in relation to differing concentrations of acid and base. The Lutz and Jirgensons rule states that amino acids of the natural, or *levo*, configuration show, as the ratio of moles of acid added to moles of compound present is increased, an increasing positive or a decreasing negative rotation. Thus that isomer which was isolated from the water insoluble brucine salt, and showed a decreasing negative rotation as acidity was increased, was designated as possessing the natural configuration. In the second procedure for proof of configuration the specific *d*-amino acid oxidase was obtained in purified form from kidney tissue and incubated with both isomers. The isomer which was shown to possess the *levo* configuration according to the previous procedure was not

<sup>1</sup> Doctoral thesis No. 831, submitted December 18, 1946.

<sup>2</sup> Lutz and Jirgensons. Ber. 63, 448 (1930).

attacked by the *d*-amino acid oxidase, as no keto acid production could be detected by the sensitive 2,4-dinitrophenylhydrazine reagent. The other isomer, however, gave 100 per cent of the calculated amount of keto acid, which thus established the fact that the compound possessed the *d* or unnatural configuration.

Warburg manometric studies with the *d*- and *l*-isomers of *meta*-tyrosine showed the oxygen uptake observed with normal and scorbutic tissue paralleled the uptake observed for naturally occurring tyrosine. However, the values for *l-meta*-tyrosine were consistently lower than those observed with tyrosine itself. The rates of oxygen uptake observed with *l*-tyrosine and *l-meta*-tyrosine were in sharp contrast. The *meta*-tyrosine isomer showed very rapid uptake over the first hour, but the second and third hours of incubation resulted in no additional evidence of oxidation. Tyrosine itself, on the other hand, showed a fairly constant rate of oxygen uptake over the full three hour period. The number of atoms of oxygen absorbed per mole of tyrosine substrate added did not approach the values reported for the complete oxidation of tyrosine.

The investigation of Dakin's<sup>2</sup> 2-methyl-4-(2'-acetoxy-benzal)-5-oxazolone as a possible starting material for the synthesis of *N*-acetyl-*o*-tyrosine for resolution studies showed that his supposed azlactone was 3-keto-coumarin. Through conversion of the coumarin to trans- $\alpha$ -acetamido-*o*-hydroxycinnamic acid and subsequent reaction of this compound with acetic anhydride, 2-methyl-4-(2'-acetoxybenzal)-5-oxazolone was synthesized. The product was shown to be different from the azlactone claimed by Dakin. Although the trans- $\alpha$ -acetamido-*o*-hydroxycinnamic acid was converted to the desired *N*-acetyl-*o*-tyrosine by catalytic reduction, the compound was found more readily available through application of the modified Erlenmeyer synthesis used in the preparation of *meta*-tyrosine. To prevent coumarin formation, the methyl ether of salicylaldehyde was used in the preparation of the azlactone intermediate. The over-all yield of amino acid obtained was 47 per cent.

The resolution of *o*-tyrosine, through the use of the *N*-formyl derivative according to the procedure used successfully in the isolation of the isomers of *m*-tyrosine, could not be accomplished. The rotations of the brucine salts obtained from a series of solvents were so similar as to indicate that no separation of isomers was taking place. With the *N*-acetyl derivative of *o*-tyrosine, however, a salt was obtained from ethyl alcohol which showed an increasing negative rotation on repeated recrystallization. From this brucine salt, after a constant rotation was reached on recrystallization, was isolated a dextrorotatory amino acid. As this amino acid showed a decreasing positive rotation as the ratio of acid was increased, it possessed the unnatural configuration. The alcohol soluble isomer could be recrystallized only from ethyl acetate. The yield of amino acid was very poor and the procedure laborious.

The synthesis of 2,5-dihydroxyphenylalanine was undertaken in view of its relationship to homogentisic acid and its postulated role as an

<sup>2</sup> Dakin. Jour. Biol. Chem. 82, 439 (1929).

intermediate in tyrosine metabolism. The amino acid obtained through application of the modified Erlenmeyer method previously applied, gave a product which agreed in properties with those given for the molecule by Schaaf and Labouchère<sup>4</sup>. The melting point given by Hirai<sup>5</sup> of 205° was too low as our value, in agreement with Schaaf and Labouchère, was 243°. The hydantoin of the amino acid was prepared and analysed, to further establish the nature of the product. The analytical data were in agreement with the theoretical nitrogen content. An independent synthesis of 2,5-dihydroxyphenylalanine was attempted through a procedure the first step of which involved the condensation of 2-hydroxy-5-nitrobenzyl chloride with ethyl acetamidomalonate. The ethyl  $\alpha$ -acetamido-2-hydroxy-5-nitrobenzyl malonate obtained was converted readily through hydrobromic acid hydrolysis to 2-hydroxy-5-nitrophenylalanine. Reduction of this compound to 2-hydroxy-5-aminophenylalanine was accomplished with tin and hydrochloric acid. Diazotization and subsequent hydrolysis of the diazonium salt did not yield 2,5-dihydroxyphenylalanine. No crystalline product could be isolated in the investigation of several methods.

The modified Erlenmeyer method was successful in the conversion of 2-phenyl-4-(2',3'-dimethoxybenzal)-5-oxazolone to 2,3-dihydroxyphenylalanine. The N-formyl derivative of this amino acid could not be resolved as the brucine salt. The reaction of hydriodic acid with 2-phenyl-4-(2',4'-dimethoxybenzal)-5-oxazolone was exceptional in that no amino acid was obtained.

<sup>4</sup> Schaaf and Labouchère. *Helv. chim. acta*, 7, 357 (1924).

<sup>5</sup> Hirai. *Biochem. Z.* 189, 88 (1927).

# SOME SUBSTITUTED 3-INDOLEACETIC ACIDS<sup>1</sup>

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A series of substituted derivatives of 3-indoleacetic acid, a naturally occurring plant growth hormone, was prepared in order to determine the effect of the substituents upon the plant growth activity. Chloro and nitro groups were introduced; other workers had found that these groups markedly increased the plant growth activity of phenoxyacetic and benzoic acids.

The Fischer Indole Synthesis, whereby a phenylhydrazone under the influence of an acidic reagent splits out a molecule of ammonia and forms an indole ring, was employed for the preparation of substituted acids. Cyclization was brought about by mixing a substituted phenylhydrazone with five times its weight of anhydrous zinc chloride and by heating at temperatures ranging from 100° to 170°. The product obtained in this manner was extracted with ether, and saponified with alcoholic potassium hydroxide after the ether was removed. The free acid was obtained by acidification and extraction with ether. Using this general method the following compounds were prepared.

3-(2-Methyl-7-chloroindole)-acetic acid, m.p. 164°–164.5°, was obtained in 33 per cent yield from ethyl levulinate *o*-chlorophenylhydrazone, m.p. 58.5°–59.5°, by heating at 100° for one hour.

3-(2-Methyl-5-chloroindole)-acetic acid, m.p. 190° (dec.) was prepared in 44 per cent yield from ethyl levulinate *p*-chlorophenylhydrazone, m.p. 104°–106°, by heating at 125°–135° for one hour.

3-(2-Methyl-5,7-dichloroindole)-acetic acid, m.p. 215° (dec.), was obtained in 43 per cent yield from ethyl levulinate 2,4-dichlorophenylhydrazone, m.p. 74°–76° (dec.), by heating at 165°–170° for one hour.

A modification of the above procedure was used to prepare 3-(2-methyl-7-nitroindole)-acetic acid, m.p. 265° (dec.). Ethyl levulinate *o*-nitrophenylhydrazone, m.p. 59.5°–60°, was boiled with concentrated hydrochloric acid saturated with zinc chloride for one hour. The product was worked up in the usual manner and gave a 28 per cent yield of the acid.

3-Indoleacetic acid was prepared from glutamic acid in 30 per cent yield. Langheld's method, employing sodium hypochlorite as the oxidizing agent, was adapted for the preparation of larger quantities of  $\beta$ -formylpropionic acid from glutamic acid. The semi-aldehyde was converted into the phenylhydrazone. Alcoholic sulfuric acid was used to bring about ring closure.

<sup>1</sup> Doctoral thesis No. 837, submitted March 19, 1947.

The plant growth activity of the compounds prepared above was determined by the Pea Test. The following results were obtained:

3-(2-Methyl-5-chloroindole)-acetic acid was active at concentrations of 20.0, 10.0, 5.00, 2.00 and 1.00 mg. per liter.

3-(2-Methyl-7-chloroindole)-acetic acid was active at concentrations of 20.0, 10.0 and 5.00 mg. per liter.

3-(2-Methyl-5,7-dichloroindole)-acetic acid was active at concentrations of 20.0 and 10.0 mg. per liter.

3-(2-Methyl-7-nitroindole)-acetic acid was inactive at the concentrations tested, 20.0, 10.0, 5.00, 2.00 and 1.00 mg. per liter.

An attempt to prepare 3-(7-nitroindole)-acetic acid from  $\beta$ -formylpropionic acid *o*-nitrophenylhydrazone, m.p. 155°–156° (dec.), using sulfuric acid was unsuccessful. The hydrazone, when reacted with alcoholic hydrogen chloride, gave ethyl  $\beta$ -formylpropionate *o*-nitrophenylhydrazone, m.p. 75°–75.5°. The ester also failed to give the desired acid when cyclized with zinc chloride.

The preparation of 3-(5-nitroindole)-acetic acid from  $\beta$ -formylpropionic acid *p*-nitrophenylhydrazone, m.p. 185°–186°, using alcoholic sulfuric acid, was not successful.

$\beta$ -Formylpropionic acid 2,4-dichlorophenylhydrazone, m.p. 181°–182°, when treated with alcoholic hydrogen chloride, yielded a compound which melted at 215°–216° (dec.) and did not give the correct nitrogen analysis for either ethyl  $\beta$ -formylpropionate 2,4-dichlorophenylhydrazone or ethyl 3-(5,7-dichloroindole)-acetate. Cyclization of the hydrazone with alcoholic sulfuric acid also failed.

An attempt to prepare 3-(7-chloroindole)-acetic acid from  $\beta$ -formylpropionic acid *o*-chlorophenylhydrazone, m.p. 176.5°–178.5° (dec.), by cyclization with alcoholic sulfuric acid was unsuccessful.

Several compounds, which appeared to be similar to the anhydride that Fischer prepared from levulinic acid phenylhydrazone, were obtained in the course of the investigation; the corresponding derivative of  $\beta$ -formylpropionic acid *o*-nitrophenylhydrazone melted at 101.5°–102°, and the derivative of  $\beta$ -formylpropionic acid phenylhydrazone melted at 94°–95°.

# THE GENERALIZED LAPLACE TRANSFORMATION WITH APPLICATIONS TO PROBLEMS INVOLVING FINITE DIFFERENCES<sup>1</sup>

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The generalized Laplace transformation defined by the infinite series.

$$(1) \quad L \left\{ F(t) \right\}_E = f(s) = \sum_{n=0}^{\infty} \frac{F(n)}{s^{n+1}}, \quad E^m F(t) = F(t+m),$$

has many of the advantages for the calculus of finite differences that the regular Laplace transformation has for the ordinary calculus. That is, by means of the equations,

$$(2) \quad L \left\{ E^m F(t) \right\}_E = s^m f(s) - \sum_{k=0}^{m-1} s^{m-1-k} F(k),$$

$$(3) \quad L \left\{ \Delta^m F(t) \right\}_E = (s-1)^m f(s) - \sum_{k=0}^{m-1} (s-1)^{m-1-k} F(k), \quad \Delta = E - 1,$$

a simultaneous system of linear difference equations may be reduced to a simultaneous linear algebraic system without the introduction of extraneous constants. In general the transformation (1) will transform a class of functions into an essentially more simple class.

The necessary and sufficient condition that  $F(t)$  possess a generalized Laplace transform is that it be of exponential order,  $F(t) < M\alpha^t$ ,  $t > T$ , and is defined at all integral points. The infinite series (1) will converge uniformly for  $|s| > \alpha_0 > \alpha$  and the transform  $f(s)$  must be regular at

infinity. Under these conditions the power series in  $\frac{1}{s}$  may be differ-

entiated term by term with respect to  $s$  so a system of difference equations with rational coefficients may be changed to a system of differential equations by the formula

$$(4) \quad L \left\{ t^{(m)} F(t) \right\}_E = \left( -\frac{d}{ds} \right)^m s^m f(s), \quad t^{(m)} = t(t-1) \dots (t-m+1).$$

The inverse generalized Laplace transformation may be evaluated

<sup>1</sup> Doctoral thesis No. 857, submitted June 9, 1947.

by the usual partial fraction expansion of the transform  $f(s)$  but the complex inversion integral is more elegant. Given that

$$(5) \quad F(t) = L^{-1} \{f(s)\}_t$$

then

$$(6) \quad F(t) = \frac{1}{2\pi i} \int_C z' f(z) dz,$$

where the contour of integration is a closed curve which encloses the singular points of  $f(s)$ . It follows then that

$$(7) \quad F(t) = \text{sum of the residues of } s'f(s).$$

Multiplication of the two series which define  $f(s)$  and  $g(s)$  yields the convolution summation which corresponds to the faltung integral of the regular Laplace theory:

$$(8) \quad L^{-1} \{f(s)g(s)\}_t = \sum_{n=0}^{t-1} F(t-n-1)G(n).$$

The differential equations which describe an irregular physical system may often be replaced by difference equations which lend themselves more readily to a numerical solution. The  $M$  transformation,

$$(9) \quad L \{F(k)\}_M = f(s) = 2 \sum_{n=0}^{\infty} \frac{F(n)}{s^{n+1}} - \frac{F(0)}{s},$$

is linearly related to the generalized Laplace transformation and is designed for the solution of difference equations which arise from the substitutions,

$$(10) \quad \begin{aligned} x &\rightarrow hk, \\ \frac{d}{dx} F(x) &\rightarrow \frac{M}{h} F(k) = \frac{F(k+1) - F(k-1)}{2h}, \\ \frac{d^2}{dx^2} F(x) &\rightarrow \frac{\Delta^2}{h^2} F(k) = \frac{F(k+1) - 2F(k) + F(k-1)}{h^2}, \end{aligned}$$

where  $h$  is the finite difference interval and  $k$  takes on integral values. Application of (9) yields the solution of the difference equations which are usually obtained by laborious solution of a system of simultaneous equations. The inverse transforms are best evaluated by the complex inversion integral,

$$(11) \quad F(k) = \frac{1}{2\pi i} \int_C \frac{z^k}{2} \left[ f(z) + \frac{F(0)}{z} \right] dz,$$

or by the convolution summation,

$$\begin{aligned}
 (12) \quad L^{-1} \left\{ f(s) g(s) \right\}_M &= 2 \sum_{n=0}^{k-1} F(k-n-1) G(n) - \frac{G(0)}{s} f(s) \\
 &\quad - \frac{F(0)}{s} g(s) - \frac{F(0) G(0)}{s^2}.
 \end{aligned}$$



# THE EFFECT OF NITROGEN FERTILIZATION ON THE NITROGEN NUTRITION OF LEGUMES<sup>1</sup>

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Methods heretofore employed in the study of nitrogen fixation by legumes have not been entirely satisfactory. Most have been indirect in their approach, and as a result a great deal of confusion exists in the literature on the subject. Recently the introduction and use of isotopic tracers in the study of plant and animal nutrition has greatly facilitated the acquisition of more reliable information. The employment of the stable nitrogen isotope of mass 15 has made it possible to determine the exact source of nitrogen in leguminous plants, thus giving an accurate appraisal of the fixation process.

Greenhouse experiments designed to study the effects of nitrogen fertilization on nodulation, yield, nitrogen content and nitrogen fixation by inoculated legumes were conducted over a period of 18 months. N<sup>15</sup> enriched nitrogen was used in 3 experiments with soybeans and one experiment with lespedeza, sweet clover, red clover and peanuts. Ordinary nitrogen was used in experiments with sweet clover, lespedeza, red clover, white Dutch clover and peanuts. Several sources of nitrogen were used in the various experiments.

Nitrogen in the form of calcium nitrate was applied to soybeans, lespedeza, white Dutch clover, sweet clover and peanuts at the time of planting and approximately 5 weeks after planting. Sodium nitrate and ammonium sulfate at rates of 20 and 60 p.p.m. were applied to red clover at planting and 10 and 20 days after planting. Potassium nitrate was applied to soybeans and sweet clover at planting and to soybeans 5 weeks after planting in a sand-clay culture.

Plants were harvested approximately 6 and 11 weeks after emergence. The effect of nitrogen fertilization on nodulation was determined at the early harvest by counting the number of nodules per plant and noting their size and distribution on the roots. Dry weight yields and nitrogen determinations were made for both early and late harvest. Absorption of combined nitrogen and subsequent effects on fixation were measured by determining the N<sup>15</sup> enrichment in all nitrogen samples from plants receiving this isotope.

The results of experiments with soybeans corroborate and extend previously reported data that nodulated soybeans do not make maximum growth when dependent solely on the fixation mechanism for their nitrogen supply. It was also established that the amount of nitrogen fixed by soybeans is related inversely to the amount of available combined

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<sup>1</sup> Doctoral thesis No. 844, submitted June 5, 1947.

nitrogen present in the soil. Fifty p.p.m. of nitrogen applied at planting had a greater depressing effect on fixation than 25 p.p.m. applied at the same time. The same was true for midseason applications; however, both rates were less effective in depressing fixation than were applications made at planting. In all cases where nitrogen was applied the total nitrogen content of the plants was increased above that found in plants receiving no nitrogen. A greater portion of the nitrogen added at planting was recovered in the tops and roots, whereas, when the addition was made at midseason the larger portion was found in the seed. Nitrogen applied at planting greatly depressed nodulation; however, when the plants were harvested 5 weeks after emergence it was found that approximately 50 per cent of the total nitrogen content was from fixation even though a near ample supply of combined nitrogen was present.

When calcium nitrate enriched with  $N^{15}$  was applied to lespedeza it was found that the added nitrogen had no appreciable effect on fixation during the first 9 weeks of growth. However, when the plants were harvested 14 weeks after emergence all nitrogen treatments had depressed fixation. Fixation was depressed more by applications of nitrogen made at planting than by midseason applications.

Red clover and sweet clover yields and nitrogen contents were increased by nitrogen fertilizers. Red clover plants, receiving 60 p.p.m. of nitrogen at planting as ammonium sulfate with  $N^{15}$  enrichment and harvested 6 weeks after emergence, fixed more nitrogen than plants receiving no nitrogen. Nitrogen applications as sodium nitrate at planting and 20 days after planting and ammonium sulfate 20 days after planting reduced fixation. Sixty p.p.m. of nitrogen as ordinary sodium nitrate resulted in yields of dry matter superior to the 20 p.p.m. rate for all dates of application when the tops of red clover were harvested approximately 66 days after emergence. Twenty p.p.m. of nitrogen as ammonium sulfate at planting gave equally as satisfactory yields as the higher rate of sodium nitrate for all dates of application. Total nitrogen content of plants receiving the larger rate of sodium nitrate at all three times of applying were significantly better than that obtained when no nitrogen was added or when 20 p.p.m. were added. Twenty p.p.m. of nitrogen as sulfate of ammonia at planting and 60 p.p.m. at planting and 10 days after planting resulted in plants having nitrogen contents comparable to those obtained from the larger rates of sodium nitrate; whereas, the smaller rate of ammonium sulfate at 10 days after planting and both rates 20 days after planting were without significant effect on nitrogen content.

When sweet clover, receiving 15 p.p.m. of nitrogen as ordinary calcium nitrate at planting, 15 p.p.m. 5 weeks after planting, and 15 p.p.m. at planting plus 15 p.p.m. 5 weeks after planting, was harvested 11 weeks after emergence it was found that there was a net increase in nitrogen content above that found in plants receiving no nitrogen plus the added amount. This indicated that fixation had been enhanced by the added nitrogen.

White Dutch clover was adversely affected by applications of calcium

nitrate at the rates of 10 and 20 p.p.m. either at planting or 5 weeks after planting.

Peanuts responded favorably to applications of calcium nitrate. Six and 12 p.p.m. of nitrogen applied at planting and 5 weeks after planting favored early maturity of fruit, whereas, excessive amounts of combined nitrogen somewhat delayed maturity.

When potassium nitrate was added to sweet clover and soybeans in sand-clay cultures at varying calcium saturation levels nodulation of the two species was affected somewhat differently. In the case of sweet clover the nodules on plants receiving combined nitrogen were small, very numerous and distributed over the lateral roots; whereas, with soybeans there was an almost complete inhibition of nodules as a result of nitrogen applications at planting.

Fixation of nitrogen by the two plants also differed. In the case of the sweet clover fixation was depressed during the first 5 weeks of growth but at 11 weeks it was found that fixation had been greatly enhanced by nitrogen applications. Fixation by soybeans was significantly depressed at low and medium calcium levels and slightly but not significantly reduced at the high calcium level.

Employing a technique whereby the rooting and fruiting zone of peanut plants were separated, combined with the use of  $N^{15}$  it was established that nitrogen absorption takes place through the gynophores. The amount of nitrogen taken in, in this manner, was related to the amount of available nitrogen in the rooting zone. In plants having access to an ample supply of nitrogen in the root zone either in a combined form or from nodulation only 29 per cent of the nitrogen applied to the fruiting zone was recovered; whereas, when a near nitrogen starvation level existed at the rooting zone recovery from the fruiting area was in excess of 98 per cent of that added.

# A COMPARISON OF SOME LABORATORY METHODS FOR THE PRODUCTION OF ANTIBODIES<sup>1</sup>

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The purposes of this investigation were to obtain more information regarding the nature of antibody formation and to develop a simple procedure for evoking precipitating antibodies.

Many hypotheses of the mechanism of antibody formation have been suggested. They may be divided into two general proposals. One concept is that antibody production is a synthetic function of cellular systems. The second proposal is that antibodies may be produced by altering the stereochemical and/or electrochemical properties of non-antibody proteins; no synthetic mechanism is postulated.

The following chemically modified proteins were prepared for use as antigens: 3,5-diiodo-4-hydroxybenzeneazo casein, 4-sulfobenzeneazo casein, 4-carboxybenzeneazo casein, nitro casein, guanidyl casein, guanidyl egg albumen, and the iodo and 4-arsonobenzeneazo derivatives of casein, egg albumen, and crystalline plasma albumin. The proteins were purified by reprecipitation and by dialyses against distilled water, were dried over sulfuric acid in a vacuum desiccator for seven days, and were analyzed for characteristic elements such as arsenic, iodine, nitrogen and sulfur.

Recently, there have been two reports of the production of antibodies by *in vitro* incubation of blood plasma or serum with antigenic materials. Pauling and Campbell<sup>2</sup> prepared antibodies *in vitro* by heating mixtures of normal globulins and antigens to 65° C., slowly cooling, and incubating for several days at 57°. The mixtures were then dialyzed against a 1 per cent solution of sodium chloride to remove excess antigen. Aliquots of the dialyzates gave weak but specific precipitin tests. Bacon<sup>3</sup> reported the production of antibodies to diphtheria and staphylococcus toxins by a method similar to that of Ostromuiskii<sup>4</sup>. A mixture of bovine plasma and toxin (2 per cent by volume of toxin) was lyophilized, and the dried material was incubated for twelve hours at 37°. The plasma was then restored to its original volume and pH and tested for precipitin content.

In the present study, the observation of antibody formation by incubation of plasma and antigens *in vitro* was extended to the formation of precipitins for chemically modified proteins. By the use of a slight modification of Bacon's procedure, precipitins were prepared for such

<sup>1</sup> Doctoral thesis No. 828, submitted December 17, 1946.

<sup>2</sup> Pauling and Campbell, *Sci.* 95, 440 (1942); *J. Exptl. Med.* 76, 211 (1942).

<sup>3</sup> Bacon, *Arch. Internal Med.* 72, 581 (1943).

<sup>4</sup> Ostromuiskii, *J. Russ. Phys. Chem. Soc.* 47, 263 (1915).

antigens as 3,5-diiodo-4-hydroxybenzeneazo casein, iodo casein, 4-arsonobenzeneazo casein, iodo egg albumen, and 4-arsonobenzeneazo egg albumen. Precipitins could be demonstrated in 90 per cent of the 21 preparations studied. Cross tests indicated specificity of reaction in approximately two-thirds of the preparations. The antigens containing arsenic or iodine were the most satisfactory of the antigens studied in causing production of antibodies, in regard to both strength and specificity of precipitin reactions.

In attempts to develop a rapid method for production of the relatively large amounts of antibodies which are needed for chemical studies of antibody composition, yeast was tested because of its rapid synthesis of protein as demonstrated in the manufacture of nutritional concentrates<sup>5</sup>.

There are few reports in the literature on the production of antibodies by microorganisms. Rosenow<sup>6</sup> obtained substances resembling agglutinins from streptococci, pneumococci, staphylococci, and *B. subtilis* suspensions which had been autoclaved for 48 hours at 17 pounds pressure in 0.5 N acid solution. Deutschmann<sup>7</sup> claimed to have produced antitoxins by culturing yeast in media containing a toxin.

In the course of this study, acquired precipitins have been demonstrated in extracts of a yeast, *Saccharomyces cerevisiae*, cultured in media containing foreign proteins. The antigens tested were 4-sulfobenzeneazo casein, 4-carboxybenzeneazo casein, guanidyl casein, guanidyl egg albumen and the 4-arsonobenzeneazo and iodo derivatives of casein, egg albumen, and crystalline plasma albumin.

In the method employing *S. cerevisiae*, inocula of Strain No. 567 of the Northern Regional Research Laboratory were incubated in 100 ml. of a 15–20 per cent (g./ml.) solution of molasses for 24 hours at 30°. Aliquots of the culture containing approximately  $6 \times 10^8$  cells were transferred to fresh medium (100 ml.) containing the antigen in 0.1 per cent concentration, and were incubated for 48 hours at 30°. After incubation, the cells were separated by centrifugation, washed with water, cytolized by grinding with sea sand and ether for approximately 30 minutes, and extracted with 25 ml. of a 5 per cent solution of sodium chloride. The extracts were clarified by centrifugation and treatment for 15–20 minutes with 0.1 g. of Filter Cel. The extracts were then tested for precipitin content by Hanks' micro method<sup>8</sup>. Specific precipitin reactions were observed in 82 per cent of 17 of such preparations tested.

Extracts giving macro precipitin tests were obtained from yeast cells which were transferred to fresh media containing the same concentration of antigen each 48 hours for a total of 2 to 6 transfers, and then were cytolized and extracted by the procedure given above. In tests of extracts of 17 of such cultures, macro tests indicated the presence of specific precipitins at selected transfer levels in 14 (82 per cent) cases.

<sup>5</sup> Fink, *Vorratspflege u. Lebensmittelforsch.* 1, 51, 107 (1938).

<sup>6</sup> Rosenow, *J. Infectious Diseases* 76, 163 (1945).

<sup>7</sup> Deutschmann, *Brit. Patent* 239, 302, June 11, 1924.

<sup>8</sup> Hanks, *J. Immunol.* 28, 95 (1935).

In each culture, there was an optimal number of transfers. At some other transfer levels, weaker and less specific precipitation was noted.

Considerable variation in strength and specificity of precipitin reactions was noted in micro and macro tests of yeast extracts prepared during 16 months of experimentation.



# STUDIES ON OXYGEN-CARRYING COBALT COMPOUNDS<sup>1</sup>

## VIII. ANALOGUES OF DISALICYLALETHYLENEDIIMINE COBALT WITH *o*-HYDROXYCARBONYL COMPOUNDS OTHER THAN SALICYLALDEHYDE

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In Paper IX of this series it will be shown that substitution in or for the ethylenediamine portion of the molecule of the oxygen-carrying compound bi-(disalicylalethylenediimine)- $\mu$ -aquo-dicobalt yielded cobalt derivatives which invariably failed to absorb and release oxygen reversibly. As indicated in Papers V, VI, and VII dealing with the derivatives from 3-nitrosalicylaldehyde, 3-methoxysalicylaldehyde and various higher 3-alkoxysalicylaldehydes, substitution in the salicylaldehyde portion of the molecule is permissible, indeed beneficial in that the substituted derivatives may have a higher rate of oxygenation, lower deoxygenation temperature, and other desirable physical properties.

The present paper deals with a variety of substituted salicylaldehydes and other  $\beta$ -diketones analogous to salicylaldehyde. Most of the cobalt-ethylenediamine compounds of these  $\beta$ -dicarbonyl compounds were inactive. The few which were active absorbed oxygen slowly and failed to absorb the theoretical amount of oxygen.

The method and conditions under which the cobalt compound was formed appeared to be of great importance in determining if the material was to absorb oxygen. Consequently the method used in making each of the cobalt compounds is reported in some detail even at the risk of what might appear to be needless repetition.

Some generalizations may be drawn from this work regarding substitution. Apparently large alkyl substituents, greater than ethyl, cannot be introduced and an active product obtained; this is true for substituents both on the ring and on the aldehyde group (phenones). Not more than one substituent, alkyl, nitro, chloro, bromo, or alkoxy may be introduced. The substitution in the 3- position is favored in preference to the others but not invariably.

### ALKYL SUBSTITUENTS

The four possible methyl substituted salicylaldehydes, were synthesized from *ortho*-, *meta*-, and *para*-cresol by the Reimer-Tiemann reaction. The Schiff's base of each of these aldehydes with ethylenediamine was prepared and the cobalt derivative of each of these Schiff's bases. The

<sup>1</sup>Preceding parts of this discussion were published in this Journal as follows: Papers I, II, and III, Vol. XXI, pp. 271-309, 1947; Papers IV, V, VI, and VII, Vol. XXI, pp. 311-349, 1947.



cobalt compounds were also prepared by the direct interaction of the aldehyde, diamine, and cobalt salt in dilute alcohol.

Di-(2-hydroxy-3-methylbenzal)-ethylenediimine cobalt was prepared by the direct interaction method and also through the potassium salt of the Schiff's base. Neither of these preparations absorbed oxygen when placed in an atmosphere of oxygen at 200 pounds pressure.

Di-(2-hydroxy-4-methylbenzal)-ethylenediimine cobalt, when prepared by the direct interaction method, showed no oxygen-carrying activity. A preparation of the compound made by boiling an aqueous suspension of a mixture of the Schiff's base and a cobalt salt was active, reversibly absorbing and releasing 1.56 per cent oxygen. It did not absorb oxygen from air at atmospheric pressure and was therefore less active than the parent compound, disalicylalethylenediimine cobalt.

Di-(2-hydroxy-5-methylbenzal)-ethylenediimine cobalt was synthesized by both methods. The compound prepared by the direct interaction method carried 2.7 per cent oxygen. This compound did not absorb oxygen from the air at atmospheric pressure and was therefore less active than the parent compound. A preparation of the material through the Schiff's base was inactive.

Di-(2-hydroxy-6-methylbenzal)-ethylenediimine cobalt was prepared by the direct interaction method and was found to have an oxygen-carrying capacity of 2.34 per cent.

The work on this series of compounds was handicapped by the low yields obtained in the Reimer-Tiemann reaction on the various cresols. None of the preparations closely approached the theoretical oxygen-carrying capacity, and the active preparations failed to absorb oxygen from the air at atmospheric pressure so that these compounds appear to be of little interest. The failure to obtain an active compound with the 3-methyl aldehyde should not be regarded as conclusive. With sufficient aldehyde available, it might be possible to find conditions which would lead to an active compound. Apparently the oxygen-carrying property resides in a peculiar crystal structure and the method of formation has considerable to do with the crystal form obtained. Four dimethylsalicylaldehydes were prepared: 3,5-, 3,6-, 4,5-, and 4,6- by means of the Duff reaction on the requisite phenol. The Schiff's bases of these aldehydes with ethylenediamine were made, and the cobalt derivatives of the latter were prepared. None of the compounds were active toward oxygen.

One ethylsalicylaldehyde was prepared, 2-hydroxy-5-ethylbenzaldehyde. Its Schiff's base was crystalline and the cobalt derivative carried 3.94 per cent oxygen. Its rate of oxygenation was about that of the parent compound.

Several more highly, alkyl substituted salicylaldehydes were prepared and their ethylenediamine-cobalt derivatives studied:

- 2-hydroxy-3-methyl-5-*tert*-butylbenzaldehyde
- 2-hydroxy-4-methyl-5-*tert*-amylbenzaldehyde
- 2-hydroxy-3-*iso*-propyl-6-methylbenzaldehyde
- 2-hydroxy-3-*tert*-amylbenzaldehyde

None of the cobalt compounds carried oxygen.

The compound, formylcamphor, contains a keto group adjacent to an aldehyde group and has been shown to enolize yielding a hydroxyl group adjacent to the aldehyde group. The enol structure is similar to that found in aromatic *o*-hydroxyaldehydes. A nickel derivative of the Schiff's base of formylcamphor with ethylenediamine was prepared by Pfeiffer and Mitarb (9), but no other metal derivatives appear to have been reported. The cobalt derivative was prepared without difficulty. It was rose-red in color and melted with decomposition. It failed to absorb oxygen on being subjected to the usual tests. The cobalt derivatives of phenylenediamine and formylcamphor was also inactive.

#### HYDROXY AND METHOXY SUSTITUENTS

2,3-Dihydroxybenzaldehyde and 2,4-dihydroxybenzaldehyde yielded crystalline Schiff's bases with ethylenediamine. The cobalt derivatives of these bases were prepared and found to be inactive. 2-Hydroxy-5-methoxybenzaldehyde and 2-hydroxy-5-ethoxybenzaldehyde were synthesized from *p*-methoxyphenol and *p*-ethoxyphenol respectively by the Duff reaction. Their Schiff's bases with ethylenediamine were also yellow, crystalline materials. The cobalt derivatives were also inactive.

#### CHLORO AND BROMO SUBSTITUENTS

3-Chlorosalicylaldehyde was obtained from *o*-chlorophenol by the Duff reaction. Its Schiff's base with ethylenediamine yielded a red-brown cobalt compound which carried 1.8 per cent oxygen. The rate of absorption was very low, however.

3-Bromo and 5-bromosalicylaldehyde yielded cobalt compounds which were inactive. Four aldehydes prepared from commercially available phenols by the Duff reaction, 2-hydroxy-3-chloro-5-*tert*-butylbenzaldehyde, 2-hydroxy-5-chloro-6-methylbenzaldehyde, 2-hydroxy-3-*iso*-propyl-5-chloro-6-methylbenzaldehyde, and 2-hydroxy-3-bromo-5-*tert*-butylbenzaldehyde, were also studied. All of the cobalt compounds were inactive.

#### NITRO SUBSTITUENTS

Although the cobalt-ethylenediamine derivatives of 2-hydroxy-3-nitrobenzaldehyde (3-nitrosalicylaldehyde) was found to be an oxygen carrier (Paper V), that from 2-hydroxy-5-nitrobenzaldehyde was found to be inactive. The cobalt derivative was made by two different methods and was heated at 170° in a vacuum before testing it for activity toward oxygen. The derivatives of 2-hydroxy-3-nitro-5-methylbenzaldehyde and of 2-hydroxy-3-methoxy-5-nitrobenzaldehyde were also inactive.

#### *o*-HYDROXYPHENONES

When properly prepared the cobalt compound of *o*-hydroxyacetophenone and ethylenediamine, di-(2-hydroxyacetopheno)-ethylenediamine cobalt, was found to carry oxygen reversibly to the extent of about 4 per cent. The rate of oxygenation was very low, however, even under relatively high oxygen pressure. Since the introduction of a nitro group into the 3-position of the parent compound, disalicylalethylenediimine

cobalt, greatly increased the rate of oxygenation, the derivative of 2-hydroxy-3-nitroacetophenone was also synthesized. The compound was inactive.

2-Hydroxy-4-methylacetophenone, 2-hydroxy-5-methylacetophenone, 2,4-dihydroxyacetophenone (resacetophenone) and 2-hydroxypropio-phenone were also studied; all yielded crystalline Schiff's bases with ethylenediamine, and all of the Schiff's bases yielded cobalt derivatives without difficulty. The compounds from 2-hydroxy-4-methylacetophenone and 2-hydroxypropio-phenone were inactive. That from 2-hydroxy-5-methylacetophenone carried 1 per cent oxygen, while that from 2,4-di-hydroxyacetophenone carried 0.3 per cent oxygen after drying in a vacuum at 100° but after being heated to 170° in a vacuum was inactive.

## EXPERIMENTAL WORK

### GENERAL NOTE ON THE REIMER-TIEMANN REACTION

Tiemann and Schotten (1) described the preparation of *meta*-, *ortho*-, and *para*-cresols from the corresponding toluidines and the preparation of all of the isomeric homosalicylaldehydes (methylsalicylaldehydes) resulting from the application of the Reimer-Tiemann reaction on these cresols. All the later references to the preparation of those compounds are based on the original article cited above. During the course of the work being reported here, the preparation of these homologues was repeated several times, and the improvements made in the synthesis of these particular aldehydes justifies including a detailed account of the work even in view of the considerable general literature on the Reimer-Tiemann reaction.

The literature contains numerous references, mostly patents, to methods of separating the three isomeric cresols and to methods for the quantitative determination of one isomer in the presence of the others. However, no good laboratory procedure was found for purifying a product already 90 per cent pure, and the following work was done on technical grade cresols carefully fractionated in vacuum.

### 2-HYDROXY-5-METHYLBENZALDEHYDE

*p*-Cresol, Eastman Kodak Company P-449, a black liquid at room temperature, was fractionated under vacuum. The product was colorless and crystallized upon standing at room temperature; m.p.: 35°, reported m.p.: 36°. A mixture of 140 g. of potassium hydroxide, 45 g. of *p*-cresol, and 300 ml. of water was heated just to boiling in a 1 l. flask fitted with a reflux condenser. By means of a dropping funnel 80 g. of chloroform was added at such rate that the reaction mixture boiled gently. This addition required about 45 to 60 minutes, during which the color gradually changed from yellow to orange and to dark red. The reaction mixture was then refluxed for 3 hours and then acidified with 175–200 ml. of concentrated hydrochloric acid. The mixture was distilled until the distillate was clear. A yellow oil separated from the milky distillate.

The distillate was extracted with one 100 ml. portion and two 50 ml.

portions of ether. The ether extract was then shaken with two 100 ml. portions of a 10 per cent sodium bisulfite solution, followed by a third extraction with the same volume of a warm 20 per cent bisulfite solution, and then with 25 ml. of distilled water.

The bisulfite extract was then placed in a flask connected to a steam generator and fitted with a dropping funnel. A suction flask was used for a receiver and was connected to a water aspirator and a gentle suction applied to carry away the sulfur dioxide gas formed in the ensuing reaction. Fifty ml. of concentrated sulfuric acid was added through the dropping funnel. After the evolution of sulfur dioxide had subsided the solution was steam distilled. The 2-hydroxy-5-methylbenzaldehyde was collected in the receiver as a light yellow oil which crystallized readily on cooling. It was filtered off. An ether extract of the filtrate showed but a trace of the aldehyde and hence further extraction was not necessary. The solution remaining from the bisulfite extraction was evaporated to remove ether, and the remaining cresol was recovered.

The 2-hydroxy-5-methylbenzaldehyde was recrystallized by dissolving it in a minimum of hot ethyl alcohol, then adding about an equal volume of distilled water, and heating until the milkiness disappeared leaving a clear solution. The solution was then allowed to cool to room temperature, whereupon beautiful, glistening, white plates were obtained. The solution was cooled in ice, filtered, washed on the filter with a small portion of ice-cold ethyl alcohol, and dried by suction in air. Yield: 15 per cent; m.p. crude product: 52°–53°; after first recrystallization: 54°; after second recrystallization: 55.8°; reported by Tiemann and Schotten (1): 56°.

A lower yield was obtained when the reaction mixture was allowed to stand a considerable length of time (overnight or weekend) before acidification and steam distillation. This may be due to polymerization of the aldehyde when remaining in contact with the concentrated alkali.

This aldehyde was also synthesized by the Duff reaction (5,6); yield: 30 per cent; m.p.: 54°.

#### DI-(2-HYDROXY-5-METHYLBENZAL)-ETHYLENEDIIMINE

To 4.3 g. (0.05 mole) of 68.7 per cent ethylenediamine dissolved in 200 ml. of water was added 18.6 g. of 2-hydroxy-5-methylbenzaldehyde dissolved in 400 ml. of 95 per cent ethyl alcohol warmed to 60°. A yellow precipitate formed immediately which was filtered off and recrystallized once from 95 per cent ethyl alcohol and twice from a mixture of benzene and petroleum ether; m.p.: 164°.

#### DI-(2-HYDROXY-5-METHYLBENZAL)-ETHYLENEDIIMINE COBALT

A quantity of 4.3 g. of ethylenediamine (68.7 per cent, 0.05 mole), was dissolved in 100 ml. of 50 per cent alcohol-water solution, and added to 12.45 g. (0.05 mole) of cobalt acetate,  $\text{Co}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 4\text{H}_2\text{O}$ , dissolved in 150 ml. of 50 per cent ethyl alcohol at 50°. A solution of 13.6 g. (0.1 mole) of 2-hydroxy-5-methylbenzaldehyde and 2 g. of sodium acetate dissolved in 200 ml. of 95 per cent alcohol was added to the cobalt-diamine solution.

The volume of solvent used was probably a little large as only a small amount of the violet-brown precipitate formed. After being shaken for 15 minutes the mixture was filtered, washed with cold, 50 per cent alcohol, and sucked dry with a sheet of thin rubber covering the precipitate in the funnel.

This violet-brown material was dried for 4 hours at 100° in a vacuum, then pulverized, yielding a fluffy, reddish-brown powder, and dried to constant weight in a vacuum at 100°.

A weighed sample of the material, placed in an atmosphere of oxygen at 200 pounds pressure became much darker brown in color, increased considerably in volume, and gained in weight 2.7 per cent, owing to the absorption of oxygen. It was readily deoxygenated in a vacuum at room temperature or at 100° at atmospheric pressure. The oxygenation cycle was repeated several times, but the oxygen-carrying capacity did not increase. On exposure to air at atmospheric pressure the material did not absorb oxygen.

A preparation of this cobalt compound made by dissolving the Schiff's base, di-(2-hydroxy-5-methylbenzal)-ethylenediimine, and two equivalents of sodium hydroxide in water and treating with the correct amount of cobalt acetate in a solution containing a little acetic acid yielded a brown precipitate which on drying at 100° in a vacuum decomposed slowly and continuously liberating 2-hydroxy-5-methylbenzaldehyde. The product did not absorb oxygen.

The failure to obtain a satisfactory oxygen-carrying product in this manner is puzzling as this method of preparation is the best in the case of the parent and other oxygen-carrying compounds.

#### 2-HYDROXY-4-METHYLBENZALDEHYDE AND 2-HYDROXY-6-METHYLBENZALDEHYDE

Tiemann and Schotten (1) reported one homosalicylaldehyde from the Reimer-Tiemann reaction on *m*-cresol. Later Chuit and Bolsing (2) isolated the expected two aldehydes and gave several possible methods for the separation of the isomers. The procedure of Chuit and Bolsing was followed in the preparation and separation of these two aldehydes.

*m*-Cresol, Eastman Kodak Company P-369, was fractionated under a vacuum, and a water-clear product was obtained; m.p.: 11°; reported m.p.: 11°–12°. Both the purified and the practical grade were used with about equal success.

A mixture of 260 g. of *m*-cresol, 1,399 g. of sodium hydroxide, and 75 g. of potassium hydroxide was dissolved in 1,000 ml. of water in a 5 l., three-necked flask fitted with a motor-driven stirrer, reflux condenser, and a dropping funnel. To the above solution was added gradually by means of a dropping funnel 248 ml. of chloroform, the addition requiring about 90 minutes. The reaction mixture was then refluxed for an additional 90 minutes and then cooled, acidified with cold dilute sulfuric acid (1:1), and steam distilled. The yellow oil which separated from the

distillate, containing the two isomeric aldehydes and unreacted cresol, was extracted with ether. The ether solution was extracted with a sodium bisulfite solution and the latter steamed distilled after acidifying just as described above in the preparation of 2-hydroxy-5-methylbenzaldehyde. A yield of 85 g. of the mixed aldehydes was obtained from two runs using 260 g. of *m*-cresol in each.

A mixture of 82 g. of the mixed isomeric aldehydes, 3.9 g. of sodium carbonate and 200 ml. of water was steam distilled until more yellow oil failed to separate from the distillate. The yellow oil which separated was isolated by means of a separatory funnel. The carbonate solution was then acidified with dilute sulfuric acid and the steam distillation continued. The second yellow oil separated upon cooling the steam distillate.

The first oil obtained could not be induced to crystallize by cooling in an ice-salt mixture. Probably this material contained a small amount of the other isomer which lowered its melting point sufficiently to make crystallization difficult. The phenylhydrazone of this aldehyde was prepared and recrystallized twice from 95 per cent alcohol; m.p.: 168°; reported by Anselmino (3): 172° for the phenylhydrazone of 2-hydroxy-6-methylsalicylaldehyde.

The second oil crystallized on cooling and was identified as 2-hydroxy-4-methylbenzaldehyde; m.p. (recry. from dilute alcohol): 59°–60°; reported (2,3): 60–61°. The phenylhydrazone was prepared and recrystallized from alcohol; m.p.: 160°, reported (3): 161°.

A mixed melting point of the phenylhydrazones of these two aldehydes melted at 134°. This leaves no question that a separation was accomplished.

#### DI-(2-HYDROXY-4-METHYLBENZAL)-ETHYLENEDIIMINE

Condensation of the aldehyde and ethylenediamine proceeded readily in alcohol. The Schiff's base was recrystallized from alcohol; m.p.: 194°.

#### DI-(2-HYDROXY-4-METHYLBENZAL)-ETHYLENEDIIMINE COBALT

To a solution containing 3.1 g. of cobalt acetate,  $\text{Co}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 4\text{H}_2\text{O}$ , and 1.1 g. of ethylenediamine in 100 ml. of 40 per cent alcohol was added a solution of 3.4 g. of 2-hydroxy-4-methylbenzaldehyde in 50 ml. of alcohol. A light brown precipitate formed in about a minute, and the mixture was shaken frequently for about 20 minutes and then filtered on a Buchner funnel, and washed with 25 ml. of 50 per cent alcohol. The product was dried at 100° in a vacuum for 3 hours, then pulverized. There was no gain in weight or change in color when subjected to oxygen at 200 pounds pressure. A sample of the compound was heated to 170° under a vacuum but was still inactive toward oxygen.

A second preparation was made by grinding together 2.9 g. of the Schiff's base and 2.5 g. of cobalt acetate with a little water. The paste was washed into a beaker, diluted to 200 ml. and heated to boiling. The yellow slurry gradually changed to a dark brown precipitate during the heating. The beaker and contents were allowed to cool somewhat and

then filtered on a Buchner funnel. The precipitate was dried for 4 hours at  $100^{\circ}$  under a vacuum, pulverized, and redried at  $100^{\circ}$  for 1 hour. After being heated at  $170^{\circ}$  in a vacuum for 2 hours, the compound carried 1.56 per cent oxygen. It was less active than the parent compound as it did not oxygenate in air at atmospheric pressure.

DI-(2-HYDROXY-6-METHYLBENZAL)-ETHYLENEDIIMINE

This Schiff's base was prepared from the liquid aldehyde described above and ethylenediamine by condensation in alcohol; m.p. after recrystallization from alcohol:  $139^{\circ}$ .

DI-(2-HYDROXY-6-METHYLBENZAL)-ETHYLENEDIIMINE COBALT

A solution of 6.8 g. of 2-hydroxy-6-methylbenzaldehyde in 25 ml. of warm 40 per cent alcohol was added to a solution of 6.2 g. of cobalt acetate,  $\text{Co}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 4\text{H}_2\text{O}$ , and 2.2 g. of ethylenediamine in 125 ml. of 40 per cent alcohol. The mixture was shaken and a heavy brown precipitate formed immediately. After standing for 30 minutes, the bulky precipitate was filtered on a Buchner funnel and washed with cold 40 per cent alcohol. The material was dried at  $100^{\circ}$  under a vacuum for 3 hours, pulverized, and dried again for 1 hour. A weighed sample was dried to constant weight at  $100^{\circ}$  under a vacuum and then placed in an atmosphere of oxygen at 200 pounds pressure. The compound turned from red to black and absorbed 2.34 per cent oxygen. It was deoxygenated at  $100^{\circ}$ . The deoxygenated form did not gain in weight upon standing in a desiccator and therefore was not as active as the parent compound. Another sample of the same preparation dried at  $170^{\circ}$  in a vacuum had an oxygen-carrying capacity of 2.2 per cent.

2-HYDROXY-3-METHYLBENZALDEHYDE

This aldehyde was synthesized from *o*-cresol by the Reimer-Tiemann reaction as described under the 5-methylaldehyde above, with the exception that the amount of sodium hydroxide used was decreased somewhat. The yield was very poor and the yellow oil obtained could not be induced to crystallize; reported m.p.:  $17^{\circ}$ . The phenylhydrazone derivative was prepared; m.p.:  $93^{\circ}$ , reported (4):  $97^{\circ}$ .

DI-(2-HYDROXY-3-METHYLBENZAL)-ETHYLENEDIIMINE

Two equivalents of 2-hydroxy-3-methylbenzaldehyde and one of ethylenediamine were condensed in ethyl alcohol yielding a bright yellow Schiff's base, m.p.:  $111^{\circ}$ . The potassium salt of this base was also prepared.

DI-(2-HYDROXY-3-METHYLBENZAL)-ETHYLENEDIIMINE COBALT

To a solution of 6.8 g. of 2-hydroxy-3-methylbenzaldehyde dissolved in 25 ml. of 50 per cent alcohol warmed to  $60^{\circ}$  was added a solution of 6.2 g. cobalt acetate,  $\text{Co}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 4\text{H}_2\text{O}$ , and 2.2 g. of ethylenediamine in 125 ml. of 50 per cent alcohol. A brown precipitate formed in a few

minutes. The flask was frequently shaken for 15 minutes, and the precipitate was filtered, washed with cold 40 per cent alcohol and dried for 3 hours at 100° under a vacuum. The material was pulverized and again dried. The product did not gain in weight or change in color when placed in oxygen at 200 pounds pressure. A second sample after being heated at 170° in a vacuum was inactive toward oxygen.

In a second preparation of this cobalt compound 5 g. of the Schiff's base and 1 g. of sodium acetate were dissolved in 150 ml. of water at 90° and treated with a solution of 2.5 g. of cobalt sulfate,  $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ , dissolved in 50 ml. of warm water. A brown precipitate formed which was filtered on a Buchner funnel and washed with 100 ml. of cold water. The compound was dried at 100°. This material and a portion of it heated to 170° in vacuum did not increase in weight in oxygen at 200 pounds pressure.

#### 2-HYDROXY-3-NITRO-5-METHYLBENZALDEHYDE

2-Hydroxy-5-methylbenzaldehyde, m.p.: 54°, was nitrated in acetic acid; m.p.: 139°; reported by Borsche (7): 141°.

#### DI-(2-HYDROXY-3-NITRO-5-METHYLBENZAL)-ETHYLENEDIIMINE

The condensation was effected in absolute alcohol on warming. Orange-yellow crystals; m.p.: above 225°. When treated with alkali this material yielded a blood red solution from which the orange-yellow Schiff's base was precipitated on acidifying. The range of pH over which the material changed color was 5.3 to 7.5, the color change being similar to that of methyl orange.

#### DI-(2-HYDROXY-3-NITRO-5-METHYLBENZAL)-ETHYLENEDIIMINE COBALT

Because of the insolubility of the Schiff's base in hot, ethyl alcohol, the cobalt derivative was prepared from a solution of the sodium salt of the base. To a solution of 10 g. of the Schiff's base and 2 g. of sodium hydroxide in 150 ml. of water, a blood red solution, was added a solution of 10 g. of hydrated cobalt chloride and 5 ml. of acetic acid in 50 ml. of warm water. The mixture was stirred and digested for 15 minutes on the hot plate. After standing 2 hours the precipitate was filtered and washed with hot water. This dark red material was dried in a vacuum at 100°, 120°, 150°, and 175° but failed to gain in weight or change in color when subjected to oxygen at 200 pounds pressure.

A second preparation of this cobalt derivative was made using hot normal propyl alcohol in which the Schiff's base is sufficiently soluble. The product was similar in appearance and inactive toward oxygen.

#### DI-(2-HYDROXY-3,5-DIMETHYLBENZAL)-ETHYLENEDIIMINE COBALT

This compound was prepared by dissolving the Schiff's base, m.p.: 132.5° (6), in hot, dilute sodium hydroxide and adding a hot, aqueous solution of cobalt chloride. A dark red material was obtained which was inactive toward oxygen.



**DI-(2-HYDROXY-3,6-DIMETHYLBENZAL)-ETHYLENEDIIMINE COBALT**

The Schiff's base, di-(2-hydroxy-3,6-dimethylbenzal)-ethylenediimine; m.p.: 182° (6), was dissolved in hot ethyl alcohol and a hot, aqueous solution of cobalt acetate added. An orange-red compound was obtained which was washed with dilute alcohol and dried in a vacuum at 120°. Found: 14.90, 14.98 per cent Co; calculated: 14.98 per cent Co. This material was heated to 175° but was inactive toward oxygen.

**DI-(2-HYDROXY-4,5-DIMETHYLBENZAL)-ETHYLENEDIIMINE COBALT**

To 10 g. of di-(2-hydroxy-4,5-dimethylbenzal)-ethylenediimine, m.p.: 212°–214° (6), dissolved in 50 ml. of water containing 1.5 g. of sodium hydroxide was added a hot solution of 8 g. of cobalt acetate in water. The compound obtained was red in color. The compound was not active towards oxygen.

**DI-(2-HYDROXY-4,6-DIMETHYLBENZAL)-ETHYLENEDIIMINE**

2-Hydroxy-4,6-dimethylbenzaldehyde was synthesized from 3,5-xilenol by the Duff reaction; yield: 11 per cent; m.p.: 48°, reported: 48°–49° (8); m.p. phenylhydrazone (from dilute alcohol): 126°; reported: 126.5°–127° (8). This aldehyde and ethylenediamine were condensed in absolute alcohol; m.p.: 152°–153°.

**DI-(2-HYDROXY-4,6-DIMETHYLBENZAL)-ETHYLENEDIIMINE COBALT**

To 15 g. of di-(2-hydroxybenzal)-ethylenediimine in 250 ml. of hot 95 per cent alcohol was added 350 ml. of a hot, aqueous solution, containing 12 g. of cobalt acetate. The compound obtained was red in color rather than the maroon tint usually associated with oxygen-carriers. After drying and activation at temperatures up to 175° the compound was found to be inactive towards oxygen.

**DI-(2-HYDROXY-5-ETHYLBENZAL)-ETHYLENEDIIMINE COBALT**

This compound was prepared by the direct mixing method in 50 per cent alcohol. A hot, aqueous solution containing 4 g. of cobalt acetate and 2 g. of 60 per cent ethylenediamine was added to 6 g. of 2-hydroxy-5-ethylbenzaldehyde (6) dissolved in alcohol. A brown compound precipitated immediately. This material was filtered off and dried in a vacuum at 115° for 1 hour. The compound absorbed 2.5 per cent oxygen in oxygen at 200 pounds pressure and turned dark in color. Upon activation at 175° the oxygen capacity increased to 3.94 per cent. The compound absorbed oxygen slowly from the air at room temperature.

**DI-(2-HYDROXY-3-METHYL-5-*tert*-AMYLBENZAL)-ETHYLENEDIIMINE COBALT**

The Schiff's base di-(2-hydroxy-3-methyl-5-*tert*-amylbenzal)-ethylenediimine, m.p.: 90° (6), was dissolved in a hot, dilute sodium hydroxide solution. To this was added a hot, aqueous solution of cobalt chloride. The compound precipitated was brick red in color but was inactive towards oxygen even after being heated to 170° in a vacuum.

DI-(2-HYDROXY-4-METHYL-5-*tert*-BUTYLBENZAL)-ETHYLENEDIIMINE COBALT

The aldehyde was synthesized from 3-methyl-4-*tert*-butylphenol by the Duff reaction (6) and may well actually be the other possible aldehyde, 2-hydroxy-5-*tert*-butyl-6-methylbenzaldehyde, rather than the 2-hydroxy-4-methyl-5-*tert*-butylbenzaldehyde indicated, or even a mixture of the two. B.p. of the aldehyde: 109°–110°/2 mm.,  $n_D^{25}$ : 1.540. M.p. of the Schiff's base with ethylenediamine: 165°. The Schiff's base was only slightly soluble in alcohol or dilute sodium hydroxide, and therefore the cobalt derivative was prepared by digesting a finely powdered suspension of the Schiff's base with a solution of cobalt acetate. An orange-red compound was obtained which was subjected to the usual tests and found to be inactive.

DI-(2-HYDROXY-3-*iso*-PROPYL-6-METHYLBENZAL)-ETHYLENEDIIMINE COBALT

The Schiff's base, di-(2-hydroxy-3-*iso*-propyl-6-methylbenzal)-ethylenediimine, m.p.: 112°–113° (6), was dissolved in a hot, dilute sodium hydroxide solution, and to it was added a hot, aqueous solution of cobalt acetate. A red compound was obtained. The compound was also prepared by adding a hot, aqueous solution containing the required amounts of cobalt acetate and ethylenediamine to a solution of the aldehyde in alcohol. A darker red compound was obtained by this method. The compounds obtained by both methods were inactive towards oxygen.

DI-(2-HYDROXY-3-*tert*-AMYLBENZAL)-ETHYLENEDIIMINE COBALT

The Schiff's base, di-(2-hydroxy-3-*tert*-amylbenzal)-ethylenediimine, m.p.: 109.5° (6) was dissolved in hot, dilute sodium hydroxide and the solution treated with a hot, aqueous solution of cobalt acetate containing a little acetic acid. A dark red compound was obtained which was not active towards oxygen.

## DI-(FORMYLCAMPHOR)-ETHYLENEDIIMINE

Formylcamphor was prepared by the method of Bishop, Claisen, and Sinclair (10). M.p.: 72°–74°; m.p. of material vacuum distilled: 80°; reported (10): 70°–76°. The condensation with ethylenediamine was effected in hot methyl alcohol. The product was slightly yellow in color; m.p.: 215°; reported (9): 215°.

## DI-(FORMYLCAMPHOR)-ETHYLENEDIIMINE COBALT

To 25 g. of the Schiff's base dissolved in 150 ml. of hot methyl alcohol was added a solution of 10 g. of cobalt acetate in 25 ml. of warm water. The mixture was digested 3 hours on a steam bath, then filtered and washed well with hot water. The product was dried in a vacuum at 100°. It was rose colored and melted at 190°–200° with decomposition. The material was inactive toward oxygen even after being further heated to 120° and 150° in a vacuum.

**DI-(FORMYLCAMPHOR)-PHENYLENEDIIMINE**

The condensation of formylcamphor and phenylenediamine was effected by bringing together warm alcohol solutions of the two. Water was added to the mixture until a slight turbidity was produced, and the solution was allowed to cool slowly. The yellow, crystalline Schiff's base which separated was filtered off, washed with water, and recrystallized from 50 per cent alcohol; m.p.: 125°.

**DI-(FORMYLCAMPHOR)-PHENYLENEDIIMINE COBALT**

The cobalt derivative of formylcamphorphenylenediimine was prepared by adding 5 g. of an aqueous cobalt acetate solution to a methyl alcohol solution containing 5 g. of the Schiff's base. A dark brown crystalline precipitate resulted which was dried in a vacuum at 100°. This material showed no change in color or gain in weight in oxygen at 175 pounds pressure. A sample was heated to 140°, but the material was still inactive.

**DI-(2,3-DIHYDROXYBENZAL)-ETHYLENEDIIMINE**

A sample of 2,3-dihydroxybenzaldehyde was obtained from the Monsanto Chemical Company; m.p.: 104°-106°; b.p.: 132°-135°/33 mm. Alcohol solutions of the necessary amounts of the aldehyde and ethylenediamine were mixed, yielding a red solution from which yellow crystals separated on cooling. After recrystallization from alcohol, this material decomposed at about 220° without melting.

**DI-(2,3-DIHYDROXYBENZAL)-ETHYLENEDIIMINE COBALT**

To a solution of 3 g. of the Schiff's base, 0.80 g. of sodium hydroxide and 0.04 g. of sodium acetate in 200 ml. of water, was added a solution of 2.37 g. of cobalt chloride in 20 ml. of water. An olive-colored precipitate formed which was filtered off, washed with water, and dried in a vacuum first at 100° and then at 170°. It was inactive toward oxygen. It was necessary to cool the material completely to room temperature before exposing it to air as otherwise spontaneous combustion occurred accompanied by a considerable display of fireworks.

Other preparations of this compound made by digesting together in suspension the Schiff's base and cobalt salt without alkali and by first preparing the pyridine addition product and depyridinating it were also inactive.

**2,4-DIHYDROXYBENZALDEHYDE**

This aldehyde was prepared by the Duff reaction (5,6). The reaction mixture after acidification with sulfuric acid was steam distilled to remove the dialdehyde as done earlier by Tiemann and Lewy (11). Only a small amount of the dialdehyde was obtained; m.p.: 127°; reported (11): 127°. The residue from the steam distillation was boiled down to a thick, red syrup which was cooled and extracted with benzene. The benzene extract

yielded white crystals of the aldehyde; m.p.: 135°–137°; reported (11): 134°–135°. Yield from 50 g. of resorcinol: 1.5 g.

DI-(2,4-DIHYDROXYBENZAL)-ETHYLENEDIIMINE

The aldehyde and the requisite amount of ethylenediamine were condensed in alcohol. Orange-yellow crystals; m.p.: above 210° (with decomp.).

DI-(2,4-DIHYDROXYBENZAL)-ETHYLENEDIIMINE COBALT

To a solution of 3 g. of the Schiff's base and 0.8 g. of sodium hydroxide in 50 ml. of water was added 2.4 g. of cobalt chloride. The brown precipitate which separated was filtered off, washed, and dried in a vacuum at 100°. It was inactive toward oxygen. A second preparation of the material was attempted in a 60 per cent alcohol solution but no precipitate formed.

2-HYDROXY-5-METHOXYBENZALDEHYDE

This aldehyde was synthesized from *p*-methoxyphenol, m.p.: 51.5°–52.5°, by the Duff reaction (5,6); m.p.: 5°; reported (5): 5°.

DI-(2-HYDROXY-5-METHOXYBENZAL)-ETHYLENEDIIMINE

The aldehyde and the required amount of ethylenediamine were condensed in alcohol; yellow crystals; m.p.: 161°.

DI-(2-HYDROXY-5-METHOXYBENZAL)-ETHYLENEDIIMINE COBALT

To a solution of 3.3 g. of the Schiff's base and 0.4 g. of sodium hydroxide in 25 per cent alcohol was added 2.4 g. of cobalt chloride. After digestion on the steam bath for 1 hour, the dark red precipitate was filtered off, washed with water, and dried in a vacuum first at 100° and then at 170°. It was inactive toward oxygen.

2-HYDROXY-5-ETHOXYBENZALDEHYDE

This aldehyde was prepared from *p*-ethoxyphenol, m.p.: 65°–66°, by the Duff reaction (5,6); yield: 16 per cent; m.p.: 48°–49°; reported (13): 51.5°.

DI-(2-HYDROXY-5-ETHOXYBENZAL)-ETHYLENEDIIMINE

The aldehyde and ethylenediamine were condensed in alcohol; yellow crystals; m.p.: 150°–152°.

DI-(2-HYDROXY-5-ETHOXYBENZAL)-ETHYLENEDIIMINE COBALT

The solubility of the Schiff's base in alcohol was so low that the cobalt derivative could not be made to crystallize from the volume necessary to dissolve the Schiff's base. Sodium hydroxide was therefore used to assist in the solution of the Schiff's base. To 3.56 g. of the Schiff's base and 0.4 g. of sodium hydroxide dissolved in 200 ml. of 25 per cent alcohol and heated to boiling was added 2.91 g. of cobalt nitrate. The mass was digested on a steam plate over night. The light-brown precipitate which formed

was filtered off, washed, and dried in a vacuum at 130°. It was inactive toward oxygen.

DI-(2,3-DIHYDROXY-5 (6?) -*tert*-BUTYLBENZAL)-ETHYLENEDIIMINE COBALT

The aldehyde was obtained from *p-tert*-butylcatechol by the Duff Reaction (5,6); it may be either the 5-*tert*- or the 6-*tert*-butyl or possibly a mixture of the two. M.p.: 85°; m.p. of the phenylhydrazone: 160°–161°; m.p. of the Schiff's base with ethylenediamine: 226°. Sharpness of the melting point would indicate only one aldehyde. The cobalt compound was prepared from the Schiff's base in a hot, dilute sodium hydroxide solution. The brown precipitate which formed was filtered off, washed, and dried in a vacuum at 100° and at 170°. It was inactive.

DI-(2-HYDROXY-3-CHLOROBENZAL)-ETHYLENEDIIMINE

2-Hydroxy-3-chlorobenzaldehyde (synthesized from *o*-chlorophenol by the Duff reaction, m.p.: 52°) and ethylenediamine were condensed in alcohol; m.p.: 143°.

DI-(2-HYDROXY-3-CHLOROBENZAL)-ETHYLENEDIIMINE COBALT

To 2 g. of the Schiff's base dissolved in 20 ml. of alcohol was added the equivalent amount of cobalt acetate in 20 ml. of water. The red-brown material which separated was filtered off, washed with water, and dried in a vacuum at 100°. The material carried 1.15 per cent oxygen reversibly. The oxygen capacity was increased to 1.88 per cent when the material was heated in a vacuum at 150°. The rate at which this compound absorbed oxygen, however, was very low.

A second preparation made in the same way but from hot alcohol had an oxygen-carrying capacity of only 0.5 per cent.

DI-(2-HYDROXY-3-BROMOBENZAL)-ETHYLENEDIIMINE COBALT

The condensation in hot alcohol of 2-hydroxy-3-bromobenzaldehyde (prepared by the Duff reaction, m.p.: 49°) and ethylenediamine yielded a yellow Schiff's base; m.p.: 174°.

DI-(2-HYDROXY-3-BROMOBENZAL)-ETHYLENEDIIMINE COBALT

To 4.25 g. of the Schiff's base and 0.8 g. of sodium hydroxide dissolved in 200 ml. of water was added a hot solution of 2.37 g. of cobalt chloride dissolved in 200 ml. of water containing a few drops of acetic acid. A dark-brown precipitate formed quickly. This was filtered off and dried at 100°. It failed to absorb oxygen when subjected to oxygen at 200 pounds pressure. Heating to 170° in a vacuum failed to activate the material.

Further preparations of the compound were made by grinding the Schiff's base and cobalt acetate together in water and digesting and by bringing the base and cobalt salt together in 70 per cent alcohol, but both procedures led to an inactive product.

**2-HYDROXY-5-BROMOBENZALDEHYDE**

This aldehyde was prepared by the direct bromination of salicylaldehyde in acetic acid (14); m.p.: 104°–106°; reported (14): 104°–105°.

**DI-(2-HYDROXY-5-BROMOBENZAL)-ETHYLENEDIIMINE**

The condensation of the aldehyde and diamine was effected in absolute alcohol. The yellow crystals were recrystallized from alcohol; m.p.: 188°–188.5°.

**DI-(2-HYDROXY-5-BROMOBENZAL)-ETHYLENEDIIMINE COBALT**

To a solution of 4.25 g. of di-(2-hydroxy-5-bromobenzal)-ethylenediimine in 100 ml. of hot alcohol was added 2.49 g. of cobalt acetate dissolved in 40 ml. of hot water. The red-brown precipitate which formed immediately was filtered off and washed with water. On drying at 100° the color of the precipitate changed to a brownish yellow. The material did not gain in weight when subjected to oxygen at 200 pounds pressure.

A second preparation made in absolute alcohol from the potassium salt of the Schiff's base and anhydrous cobalt chloride yielded the dark-yellow material directly. It was inactive toward oxygen.

Neither of these preparations lost weight on further heating to 170° in a vacuum, and neither became active.

**DI-(2-HYDROXY-3-CHLORO-5-*tert*-BUTYLBENZAL)-ETHYLENEDIIMINE COBALT**

This compound was prepared by dissolving the Schiff's base, di-(2-hydroxy-3-chloro-5-*tert*-butylbenzal)-ethylenediimine, m.p.: 115° (6), in a hot, 70 per cent alcohol and adding the requisite quantity of cobalt acetate in a hot, aqueous solution. The compound was isolated, dried, and tested in the usual manner and found to be inactive.

**DI-(2-HYDROXY-3-*iso*-PROPYL-5-CHLORO-6-METHYLBENZAL)-ETHYLENEDIIMINE COBALT**

This compound was prepared from the Schiff's base, di-(2-hydroxy-3-*iso*-propyl-5-chloro-6-methylbenzal)-ethylenediimine, m.p.: 171° (6), and cobalt acetate by adding a solution of the base in sodium hydroxide to an aqueous solution of the salt. After digestion the precipitate was filtered, washed, and dried at 100°. It was inactive even after being heated to 175°.

**DI-(2-HYDROXY-5-CHLORO-6-METHYLBENZAL)-ETHYLENEDIIMINE COBALT**

The Schiff's base, di-(2-hydroxy-5-chloro-6-methylbenzal)-ethylenediimine, m.p.: 221° (6), dissolved in alcohol was digested with a hot, aqueous solution of cobalt acetate. The final alcohol concentration was about 40 per cent. The compound was inactive.

**DI-(2-HYDROXY-3,5-DIBROMBENZAL)-ETHYLENEDIIMINE COBALT**

This compound was prepared from the Schiff's base di-(2-hydroxy-3,5-dibrombenzal)-ethylenediimine, m.p.: 247° (6). The Schiff's base was

dissolved in *n*-propylalcohol and was added to a hot, aqueous solution of cobalt acetate.

A dark brown compound formed which was filtered, washed, and dried at 100° and 175° in a vacuum. It was inactive toward oxygen.

**DI-(2-HYDROXY-3-BROMO-5-*tert*-BUTYLBENZAL)-  
ETHYLENEDIIMINE COBALT**

This compound was prepared from the Schiff's base, di-(2-hydroxy-3-bromo-5-*tert*-butylbenzal)-ethylenediimine, m.p.: 120° (6), dissolved in a dilute solution of the necessary amount of sodium hydroxide by treatment with an aqueous solution of cobalt acetate. A red compound was precipitated which was filtered, dried, and heated in a vacuum to 175° and found to be inactive.

**DI-(2-HYDROXY-5-NITROBENZAL)-ETHYLENEDIIMINE**

One-tenth mole of ethylenediamine monohydrate was added to a hot, alcohol solution of 0.2 mole of 2-hydroxy-5-nitrobenzaldehyde (see Paper V for preparation and separation from 2-hydroxy-3-nitrobenzaldehyde; m.p. after recrystallization from alcohol: 126°). A fine, yellow precipitate formed immediately which was almost insoluble in the hot alcohol. The precipitate was filtered off, washed generously with water, and dried in air; yield: almost quantitative; m.p.: above 250°. No solvent was found from which the material could be recrystallized. It was soluble in dilute potassium hydroxide.

**DI-(2-HYDROXY-5-NITROBENZAL)-ETHYLENEDIIMINE COBALT**

The Schiff's base, di-(2-hydroxy-5-nitrobenzal)-ethylenediimine, and cobalt acetate were mixed in the molecular ratio 1:1.5 and ground well together in a mortar. The mixture was then digested at 100° for 15 minutes, during which it turned dark red in color. The precipitate was filtered off, washed with water, and dried in a vacuum at 100°. A second preparation was made by treating a solution of the Schiff's base in a potassium hydroxide solution with an equivalent amount of cobalt acetate dissolved in water. In this case the cobalt compound precipitated immediately, and in nearly quantitative yield. Both preparations were heated to 170° in a vacuum but were inactive toward oxygen.

**DI-(2-HYDROXY-3-NITRO-5-METHYLBENZAL)-ETHYLENEDIIMINE**

To 28.1 g. of 2-hydroxy-3-nitro-5-methylbenzaldehyde (m.p.: 139°; prepared by nitration of 2-hydroxy-5-methylbenzaldehyde in acetic acid solution (15,16)) dissolved in 1.2 l. of alcohol, was added 6.75 g. of 68.7 per cent ethylenediamine in 300 ml. of alcohol. The orange yellow Schiff's base, which precipitated immediately, was filtered off and dried; m.p.: above 225°.

**DI-(2-HYDROXY-3-NITRO-5-METHYLBENZAL)-ETHYLENEDIIMINE COBALT**

Ten g. of the Schiff's base was dissolved in 150 ml. of hot water containing 2 g. of sodium hydroxide. To the resulting, blood-red solution was added 10 g. of cobalt chloride and 5 ml. of acetic acid in 50 ml. of warm water. The mixture was digested 15 minutes on a hot plate and the dark red precipitate then filtered off and dried in a vacuum at 100° and at 150°. The material was inactive toward oxygen.

A second preparation was made using *n*-propyl alcohol as solvent and using no sodium hydroxide. The product was also inactive.

**2-HYDROXY-3-METHOXY-5-NITROBENZALDEHYDE**

Orthovanillin was nitrated in glacial acetic acid at 10° as described by Murakini (15); m.p.: 138°–139°; reported: 138.5°–140° (15).

**DI-(2-HYDROXY-3-METHOXY-5-NITROBENZAL)-ETHYLENEDIIMINE**

To 40 g. of 2-hydroxy-3-methoxy-5-nitrobenzaldehyde dissolved in 1 l. of alcohol was added 12 g. of ethylenediamine. The yellow precipitate which formed immediately was filtered off and dried; m.p.: above 260° with decomposition.

**DI-(2-HYDROXY-3-METHOXY-5-NITROBENZAL)-ETHYLENEDIIMINE COBALT**

A fine suspension of 4 g. of the Schiff's base and 2.5 g. of cobalt acetate in 150 ml. of water was boiled for 5 minutes. The red precipitate which formed was filtered off, dried in a vacuum at 100° and at 170°, and subjected to the usual test. It was inactive toward oxygen.

**DI-(*o*-HYDROXYACETOPHENO)-ETHYLENEDIIMINE**

*o*-Hydroxyacetophenone and ethylenediamine were condensed in absolute alcohol; m.p.: 195°.

**DI-(*o*-HYDROXYACETOPHENO)-ETHYLENEDIIMINE COBALT**

The Schiff's base was dissolved in hot, 70 per cent alcohol and a hot, aqueous solution of the necessary amount of cobalt acetate added. The orange-red precipitate which formed immediately was filtered, and washed and dried at 100° in a vacuum. This compound carried about 4 per cent of oxygen reversibly but absorbed the oxygen quite slowly at room temperature even when subjected to oxygen at 200 pounds pressure.

**2-HYDROXY-3-NITROACETOPHENONE**

*o*-Hydroxyacetophenone was nitrated directly in glacial acetic acid with concentrated nitric acid. The material was isolated by steam distillation of the diluted reaction mixture. Neutralization of the acids prior to the steam distillation did not improve the poor yield nor did ether extraction of the neutralized reaction mass. The material was obtained as white needles having a barely perceptible tinge of yellow; m.p.: 97°–98°; reported: 98.5°–99.5° (18).



**DI-(2-HYDROXY-3-NITROACETOPHENO)-ETHYLENEDIIMINE**

2-Hydroxy-3-nitroacetophenone, m.p.: 97°–98°, was condensed with ethylenediamine in boiling alcohol. A quantitative yield of yellow crystals was obtained; m.p.: above 215°.

**DI-(2-HYDROXY-3-NITROACETOPHENO)-ETHYLENEDIIMINE COBALT**

Because of the insolubility of the Schiff's base in alcohol and water it was necessary to form the cobalt derivative by triturating the base with a solution of the necessary amount of cobalt acetate and warming the suspension for some time. A dark red, insoluble material was obtained which was apparently the compound desired. It did not carry oxygen after drying at 100° or at higher temperatures.

**DI-(2-HYDROXY-4-METHYLACETOPHENO)-ETHYLENEDIIMINE**

2-Hydroxy-4-methylacetophenone, synthesized from *m*-cresol acetate by the Fries reaction, b.p.: 208°/740 mm., was condensed with ethylenediamine in alcohol and the yellow Schiff's base recrystallized from *n*-propyl alcohol; m.p.: 223°.

**DI-(2-HYDROXY-4-METHYLACETOPHENO)-ETHYLENEDIIMINE COBALT**

This cobalt compound was prepared by the addition of an aqueous solution of cobalt acetate to a hot solution of the Schiff's base in *n*-propyl alcohol. A brown compound was obtained which was dried in a vacuum at 100° and at 170°. It was inactive toward oxygen.

**DI-(2-HYDROXY-5-METHYLACETOPHENO)-ETHYLENEDIIMINE**

2-Hydroxy-5-methylacetophenone was prepared from *p*-cresylacetate by the Fries reaction; yield 86 per cent, cry. p.: 45°; b.p.: 209°/740 mm. The condensation of this acetophenone and ethylenediamine was effected in alcohol, the reaction being rather slow; yellow crystals, m.p.: 198°.

**DI-(2-HYDROXY-5-METHYLACETOPHENO)-ETHYLENEDIIMINE COBALT**

This compound was prepared by the addition of a hot, aqueous solution of 2.5 g. of cobalt acetate to a solution of 7.0 g. of Schiff's base in alcohol. The red compound which formed immediately was filtered off and dried in a vacuum at 100°. When heated in a vacuum at 130° and 175° it experienced a very small loss in weight. When subjected to oxygen at 200 pounds pressure it gained 1 per cent in weight although there was no change in color. The oxygen was expelled when the material was heated to 100°. The capacity did not improve on repeated cycling. The compound was not appreciably hygroscopic since the weight remained constant upon exposure to the atmosphere for several minutes.

**DI-(RESACETOPHENO)-ETHYLENEDIIMINE**

To a solution of 11.2 g. of resacetophenone in 200 ml. of alcohol was added a cold solution of 3.61 g. of ethylenediamine in 200 ml. of alcohol. On standing a pinkish yellow precipitate formed which was filtered off and

dried. This material was insoluble in water, benzene, petroleum ether, dioxane, cyclohexane, toluene, and chloroform.

DI-(RESACETOPHENO)-ETHYLENEDIIMINE COBALT

To a solution of 5.3 g. of the Schiff's base in 150 ml. of water containing 1.5 g. of sodium hydroxide was added a solution of 9 g. of cobalt acetate in 25 ml. of water. A brownish-red precipitate formed immediately which was filtered off and dried in a vacuum at 100°. This material gained 0.3 per cent in weight in oxygen at 200 pounds pressure. After being heated to 170° in a vacuum it failed to absorb any oxygen.

A second preparation made in hot water was lighter brown in color and absorbed only 0.1 per cent oxygen after vacuum drying at 100° but again no oxygen after heating to 170° in a vacuum.

DI-(2-HYDROXYPROPIOPHENO)-ETHYLENEDIIMINE

Propiophenone, b.p.: 110°/6 mm., was condensed with ethylenediamine in alcohol. The yellow crystals obtained were recrystallized from alcohol, m.p.: 118°-118.5°.

DI-(2-HYDROXYPROPIOPHENO)-ETHYLENEDIIMINE COBALT

An attempt to prepare this cobalt compound by adding a hot aqueous solution of cobalt acetate to a hot alcoholic solution of the Schiff's base yielded only a brown oily material. Several other methods also failed to yield a solid cobalt compound.

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# STUDIES ON OXYGEN-CARRYING COBALT COMPOUNDS

## IX. ANALOGUES OF DISALICYLALETHYLENEDIIMINE COBALT WITH DIAMINES OTHER THAN ETHYLENEDIAMINE

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The intriguing property of disalicylalethylenediimine cobalt of reversibly absorbing and releasing oxygen lead naturally to an investigation of the compounds in which the ethylenediamine was replaced by other diamines. It was expected that a minor change in the composition of the compound, such as obtained by passing from ethylenediamine to propylenediamine, would modify only slightly the physical properties of the compound. Such minor modifications of the physical characteristics would be of importance from an engineering viewpoint in adapting the materials to the manufacture of oxygen; for example, a temperature of maximum rate of oxygenation of 30° would be distinctly more advantageous than one of 15° since it would permit the use of cooling water during the oxygenation phase of the cycle rather than more complicated mechanical refrigeration needed for the lower temperature.

The results were quite at variance with this simple concept, however. Of some sixteen diamines other than ethylenediamine, not one yielded a cobalt derivative which exhibited any tendency to absorb oxygen. These included diamines in which the amino groups were located on adjacent carbon atoms but in which one or more hydrogen atoms were replaced by methyl groups, and other amines in which the ethylene group was either absent (hydrazine) or replaced by  $-CH_2-$  chains of various lengths.

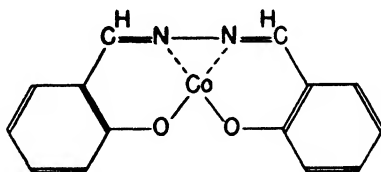
Crystalline Schiff's bases were obtained from salicylaldehyde and the majority of the diamines. These bases were invariably bright yellow in color and possessed sharp melting points.

The cobalt derivatives were generally prepared by several methods since it was shown in the case of the parent oxygen-carrying compound, disalicylalethylenediimine cobalt, that the capacity to absorb oxygen varied with the method of preparation. The preferred method was that of adding a solution of the Schiff's base in alcohol to an aqueous solution of cobalt acetate. Occasionally alkali was necessary to assist in the solution of the Schiff's bases but in those cases care was exercised to avoid excess alkali, known in the case of the parent compound, to lead to an inactive, isomeric form of the compound. Direct mixing of the diamine, salicylaldehyde and cobalt salt was also used frequently. The method of first forming a pyridine addition compound and subsequently driving off the pyridine at high temperature was also used in a number of instances.

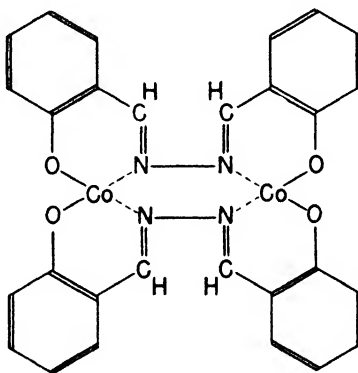
As shown in the studies of the 3-nitro and 3-methoxy derivatives of the parent compound it is sometimes necessary to expel water from the materials before they become capable of absorbing oxygen. The compounds prepared in the present investigation were therefore heated in a vacuum at temperatures as high as  $170^{\circ}$  before being abandoned as non-active.

The ability to absorb oxygen was determined by placing the materials in oxygen at 200 pounds per square inch pressure in the apparatus described in Paper XIII of this series, and noting any increase in weight.

The stereochemical implications of the failure of these compounds to absorb oxygen escape us for the present. It is unlikely in the case of the compound derived from hydrazine that the structure is



since a three membered ring would be present. More likely is the structure:



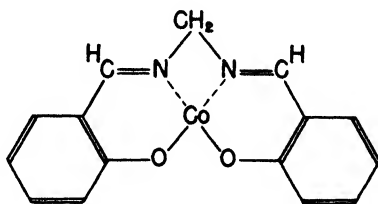
The question of the molecular weights and structure of similar compounds has been treated by Pfeiffer (1).

Of the polymethylenediamines,  $\text{H}_2\text{N}-(\text{CH}_2)_n-\text{NH}_2$ , an oxygen carrier is obtained only when  $n$  equals two, indicating that a five-membered ring must be present in the compound. In the case of the methyl substituted ethylenediamines such as propylenediamine, 2,3-butylenediamine, and tetramethylethylenediamine, a five-membered ring is present, but the compounds are inactive toward oxygen. No adequate explanation is available for this difference in behavior.

The preparation of the hydrazine compound, disalicylazine cobalt, presented no difficulty. The Schiff's base, disalicylazine, had been previously reported. The cobalt compound prepared by two methods was

found to be red brown in color, insoluble, and inactive toward oxygen. This compound was not characterized as well as might be desirable since our interest was simply in its behavior toward oxygen. This compound presents an interesting problem in stereochemistry which might well be the subject of some future investigation.

Methylenediamine,  $\text{H}_2\text{N}-\text{CH}_2-\text{NH}_2$ , would be expected to yield a Schiff's base with salicylaldehyde which would subsequently yield a cobalt compound containing a four-membered ring:



Four-membered rings are well-known in chelate ring chemistry and it is likely that the structure of the cobalt-salicylaldehyde derivative is that represented by the above formula. The instability of methylenediamine as the free base made it necessary to prepare the Schiff's base from the hydrochloride at low temperature. The cobalt derivative was prepared without difficulty.

Propylenediamine is now commercially available; indeed, the compound disalicylalpropylenediimine is marketed as an 80 per cent solution in xylene by the du Pont Company as a deactivator to remove from gasoline the metals which promote gum formation (2). Disalicylalpropylenediimine was, however, obtained as a liquid in contrast to disalicylalethylenediimine which is a beautiful, crystalline solid, melting at  $127^\circ$ . The propylenediamine was carefully fractionated and an extended purification of disalicylalpropylenediimine carried out. The final product was gummy in character, and no sharp melting point was obtained. The cobalt derivative of this material was prepared in water and in water-alcohol mixtures, but none of the products absorbed oxygen.

It was thought that the presence of an asymmetric carbon atom in the propylenediamine molecule accounted for the failure of the condensation product with salicylaldehyde to crystallize, it being known that racemic mixtures do not in general crystallize easily. For this reason it was thought that the optically active forms of propylenediamine might yield cobalt compounds which would function as oxygen carriers. Accordingly, propylenediamine was resolved by fractional crystallization of the acid tartrate. The Schiff's base, prepared directly from the acid tartrate was obtained as an oil. The cobalt derivative was found to be inactive toward oxygen.

The synthesis of disalicylalpropylenediimine cobalt through a pyridine addition product was also carried out. A crystalline pyridine addition compound was obtained, which, after drying, was heated in a vacuum at

170° to expel the pyridine. The residual material was found not to carry oxygen.

Disalicylaltrimethylenediimine was synthesized and found to be a low-melting, yellow crystalline solid. Its cobalt derivative was prepared. Analysis indicated that the material obtained was not the compound expected, but since the material obtained did not carry oxygen, it was not investigated further.

The highly symmetrically substituted ethylenediamine, tetramethylethylenediamine,  $(\text{CH}_3)_2\text{C}(\text{NH}_2)\text{C}(\text{NH}_2)(\text{CH}_3)_2$ , was obtained from the Commercial Solvents Corporation. Its identity and purity were checked and its condensation with salicylaldehyde effected in absolute alcohol. The cobalt derivative of the condensation product was prepared by several methods and numerous attempts were made to activate the compound by various heat treatments. None of the preparations functioned as an oxygen carrier.

The presence of a nitro or a methoxy group in the 3- position of salicylaldehyde has been shown to have a beneficial effect on the properties of the parent oxygen-carrying compound. It seemed possible that the presence of these groups might render the tetramethylethylenediamine compound active, and accordingly the cobalt derivatives of the condensation products of 3-nitro and 3-methoxysalicylaldehyde and tetramethylethylenediamine were prepared and subjected to the usual tests. All of the preparations were found to be inactive, thus further confirming the general conclusion that variations in the ethylenediamine portion of the parent compound always leads to a material which is not an oxygen carrier.

2,3-Butylenediamine was prepared by converting dimethylglyoxime to its diacetate by treatment with acetic anhydride, and reducing the diacetate with metallic sodium. The amine was then condensed with salicylaldehyde and the product converted into the cobalt salt. The latter was a bright-red, crystalline material which did not function as an oxygen-carrier.

The Schiff's base of hexamethylenediamine and salicylaldehyde was just as easily obtained. Several preparations of the cobalt compound were made using different procedures, but none of the products carried oxygen.

Disalicylalnonamethylenediimine, synthesized from nonamethylenediamine and salicylaldehyde, was obtained as a yellow crystalline material. Its cobalt derivative was obtained as a tar which could not be induced to crystallize. The dried and ground material was found not to carry oxygen.

Disalicylaldecamethylenediimine was synthesized and found to be a crystalline yellow solid. Its cobalt derivative was obtained as a tar which on desiccation and grinding gave a powder which was inactive toward oxygen. The materials were tested for oxygen absorption by treatment with oxygen at 100 pounds pressure as described in Paper XIII.

The aromatic base, *o*-phenylenediamine, also yields a Schiff's base with two molecules of salicylaldehyde, although it is orange in color in

contrast to the invariable yellow of the bases of aliphatic diamines. The cobalt derivative, however, did not absorb oxygen.

Several more complex amines, available commercially, were also studied; the cobalt compounds prepared were inactive toward oxygen without exception. Pentaerythrityltetramine,  $C(CH_2NH_2)_4$ , for example, condensed readily with salicylaldehyde but yielded an inactive cobalt derivative.

Diethylenetriamine,  $H_2N-C_2H_4-NH-C_2H_4-NH_2$ , and triethylenetetramine,  $H_2N-C_2H_4-NH-C_2H_4-NH-C_2H_4-NH_2$ , were condensed with salicylaldehyde and also with 2-hydroxy-3-nitro- and 2-hydroxy-5-nitrobenzaldehyde. The Schiff's bases derived from these aldehydes were viscous oils which could not be induced to crystallize. The cobalt derivatives were prepared from the oily bases but were found to be inactive. Because of the high melting points of 2-hydroxy-3-nitrobenzaldehyde and of 2-hydroxy-5-nitrobenzaldehyde, it was expected that a crystalline Schiff's base might be obtained, and this proved to be the case. The cobalt derivatives of the Schiff's bases were also more crystalline in character but were again all inactive toward oxygen. Care was taken in the case of 2-hydroxy-3-nitrobenzaldehyde to obtain a pure preparation of the aldehyde, that is, one melting about  $109^\circ$ , since, as was shown in Paper V of this series, 2-hydroxy-3-nitrobenzaldehyde having a low melting point leads to a cobalt-ethylenediamine compound inactive toward oxygen.

## EXPERIMENTAL WORK

### DISALICYLAZINE COBALT

Two equivalents of salicylaldehyde and one of hydrazine sulfate were mixed in warm alcohol. The condensation proceeded immediately forming a yellow, crystalline precipitate which was filtered off, twice recrystallized from 50 per cent alcohol, and dried. M.p.:  $216^\circ$ ; m.p. reported (3):  $213^\circ$ – $214^\circ$ ; the thermometer used was calibrated at  $212^\circ$  with anthracene, and our value is probably better.

A solution of 7.8 g. of disalicylazine dissolved in alcohol was added with vigorous stirring to a solution of 13 g. of cobalt acetate dissolved in warm water. A red-brown precipitate formed which was filtered off and dried in a vacuum at  $100^\circ$ . It did not gain in weight or change color when subjected to oxygen at 200 pounds pressure. When heated at  $150^\circ$  in a vacuum for some time it lost weight to some extent but remained inactive toward oxygen.

A second preparation of this cobalt compound made by simultaneous mixing of hydrazine sulfate, salicylaldehyde, and cobalt acetate was similar in appearance and also inactive toward oxygen.

### DISALICYLAMETHYLENEDIIMINE COBALT

A sample of methylenediamine hydrochloride was obtained from E. I. du Pont de Nemours & Co. Preliminary attempts to prepare the Schiff's base by adding sodium hydroxide to a solution of methylenediamine

hydrochloride and salicylaldehyde in absolute alcohol yielded an oil from which only a very small quantity of the base could be isolated. A reasonable yield was finally obtained by carrying out the neutralization in the cold and minimizing the heating necessary to effect the condensation. To a solution of 16 g. of sodium hydroxide in 25 ml. of water, cooled in an ice bath, was added a solution of 16.5 g. of methylenediamine hydrochloride in 25 ml. of water cooled at 0°. After 30 seconds this mixture was added to a warm solution of 48 g. of salicylaldehyde in 250 ml. of alcohol. The mixture was stirred vigorously and then allowed to cool to room temperature. On chilling further in an ice bath yellow crystals were deposited which were filtered off, washed with water, and dried. Yield: fair; m.p.: 132°. Hot solutions of this Schiff's base in alcohol had a strong odor of salicylaldehyde, indicating that it is easily hydrolyzed.

Two preparations of the cobalt derivative were made. In the first, the Schiff's base was dissolved in water containing sufficient sodium hydroxide to make the sodium salt of the base. To this was added a solution containing the equivalent amount of cobalt acetate well buffered with acetic acid and sodium acetate. The mixture was digested on a steam bath a few minutes, cooled, and filtered, and the yellow product washed with water and dried in air at 100°. The dried material was then heated in a vacuum at 170° for 2 hours and subjected to oxygen at 200 pounds pressure. It did not gain in weight or change in color. A second preparation was made using an alcohol solution of the Schiff's base with no sodium hydroxide, the volumes of the alcohol solution and the aqueous solution of cobalt acetate being so adjusted that the final reaction mixture was about 50 per cent alcohol. The product was identical in appearance and also inactive. It seemed possible that since the Schiff's base was so easily hydrolyzed that the material obtained might have been cobalt salicylaldehyde. The compound contained nitrogen, however, and an analysis for cobalt indicated that the material was undoubtedly disalicylal-methylenediimine cobalt. Found: 18.8, 18.7 per cent cobalt (evaporation with nitric and sulfuric acids and ignition at 500° to cobalt sulfate); calculated for  $C_{15}H_{12}O_2N_2Co$ : 18.9 per cent cobalt.

Unfortunately, however, this compound did not gain in weight or change in color on being subjected to oxygen at 200 pounds pressure.

#### DISALICYLALPROPYLENEDIIMINE COBALT

Commercial propylenediamine (Carbide and Carbon Chemicals Corporation) was carefully fractionated; b.p.: 115°–116°/745 mm.; reported 119°/760 mm. A sample of the distilled propylenediamine weighed in a glass stoppered bottle and opened under water was titrated with standard hydrochloric acid to the methyl red end-point. Found: 81.5 per cent propylenediamine; calculated for propylenediamine monohydrate: 80.5 per cent.

The literature contains relatively little on the Schiff's base, disalicylal-propylenediimine. Pfeiffer (4) describes the copper derivative of the compound but does not discuss the compound itself.



To 244 g. of salicylaldehyde was added 90 g. of propylenediamine slowly with vigorous stirring and cooling under running tap water. The product was a heavy, clear, yellow oil. This oil was beaten together with 300 ml. of hot water, forming a fine emulsion. After cooling and standing, the water layer was separated, carrying away any water-soluble impurity. This process was repeated with hot alcohol, in which the compound is fairly soluble. On cooling to  $0^{\circ}$ , the disalicylalpropylenediimine separated as a very viscous layer from which the alcohol was poured off. The oily layer was then heated to  $110^{\circ}$  for 30 minutes to drive off any dissolved water or alcohol. The final product was a viscous liquid. Upon standing for several days at room temperature, feathery crystals began to form. On standing for another week, the condensation product changed to a solid mass, but material having a sharp melting point was not obtained.

The cobalt compound, disalicylalpropylenediimine cobalt, was prepared by several methods. In 1.5 l. of hot water containing 15.9 g. of sodium hydroxide and 5 g. of sodium acetate,  $\text{NaC}_2\text{H}_3\text{O}_2 \cdot 3\text{H}_2\text{O}$ , was dissolved 56.6 g. (0.2 mole) of disalicylalpropylenediimine. To this solution was added with vigorous agitation a solution of 58.6 g. (0.2 mole) of cobalt nitrate,  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , in 100 ml. of hot water. The solution became yellow orange in color, and a red-brown precipitate formed on shaking and cooling to  $40^{\circ}$ . The material was centrifuged and washed with 1 l. of distilled water. The material was dried for 3 hours at  $100^{\circ}$  in a vacuum. Yield: 55 g., 81 per cent; oxygen absorption at 200 pounds oxygen pressure, room temperature: 0.05 per cent. The material was not hygroscopic.

This preparation was repeated making certain that no free alkali was present which was known to lead to an inactive red isomer in the case of the corresponding ethylenediamine compound, but again the material failed to absorb oxygen.

Another preparation was carried out in which an alcohol solution of disalicylalpropylenediimine was added to an aqueous solution of cobalt acetate, the final mixture being about 80 per cent alcohol. The addition of water did not precipitate the cobalt compound. In another preparation where the final alcohol concentration was about 50 per cent, a red-brown precipitate formed immediately. This was centrifuged from the solution washed with a large volume of water, and dried in a vacuum at  $100^{\circ}$ . The material was inactive toward oxygen.

Disalicylalpropylenediimine cobalt was also prepared through its pyridine addition compound. To 6.28 g. of propylenediamine, 22 g. of cobaltous chloride,  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ , and 36.5 ml. of pyridine dissolved in hot water was added 20 ml. of salicylaldehyde. The vessel was evacuated immediately by means of a suction pump, and evacuation was continued for 30 minutes, and at the same time the mixture was kept warm on a hot plate, the mass being shaken frequently. A dark-red precipitate formed which was filtered off after cooling, washed with cold water, pressed between filter papers at about 1,600 pounds pressure to expel liquid, and dried for several hours, in a vacuum at  $170^{\circ}$ . The material did not gain in weight when subjected to oxygen at 200 pounds pressure.

The Schiff's base of *l*-propylenediamine was prepared directly from the *l*-propylenediamine bitartrate by dissolving the latter in excess of potassium hydroxide and adding two equivalents of salicylaldehyde. Reaction occurred immediately, forming a small amount of crystalline material which was isolated and found to be inactive. The filtrate was carefully neutralized with hydrochloric acid causing the separation of an oil which on standing in contact with the mother liquor gave a further amount of a yellow crystalline material, which was found to be inactive.

The residual, red oil was washed by shaking it with water, dried, and found to be active;  $[\alpha]_D^{20} = -192.2^\circ$ . It was apparently disalicylal-*l*-propylenediimine and was used in the preparation of a cobalt compound.

Several attempts to prepare the cobalt derivative of disalicylal-*l*-propylenediimine by the addition of an alcohol solution of the active Schiff's base to an aqueous solution of a cobalt salt led to oily products of uncertain composition. A red precipitate was only obtained when the volumes of the reacting solutions were adjusted so that the final reaction mixture was less than 50 per cent alcohol. The material finally secured was similar in appearance to the oxygen carrier disalicylalethylenediimine cobalt, but was inactive toward oxygen. Even after being heated in a vacuum at  $170^\circ$  for 3 hours, a process which activates certain materials, for example di-(2-hydroxy-3-methoxybenzal)-ethylenediimine cobalt, it did not gain in weight when subjected to oxygen at 200 pounds pressure.

#### DISALICYLALTRIMETHYLENEDIIMINE COBALT

Trimethylenediamine obtained from Sharples Chemicals, Inc. was fractionated; b.p.:  $134^\circ$ – $137^\circ$ /735 mm.; reported (7):  $135^\circ$ – $136^\circ$ /738 mm. Titration with standard acid indicated that the material used contained 93 per cent of the base.

On the slow addition of 0.5 mole of trimethylenediamine to 1 mole of salicylaldehyde reaction occurred as evidenced by the generation of heat and the formation of steam. The liquid condensation product was induced to crystallize on cooling in ice. It was then dissolved in alcohol, and the concentration was so adjusted that the condensation product remained in solution until the solution was cooled below the melting point of the crystallized condensation product. To obviate the low yield obtained by this technique the major part of the Schiff's base was thrown out of the alcohol solution by the addition of ice. This slow dilution coupled with vigorous agitation gave an excellent product. The disalicylaltrimethylenediimine was finally filtered cold and dried in a desiccator which was stored in a refrigerator. The material could not be distilled under vacuum: m.p.:  $50^\circ$ – $51^\circ$ .

The cobalt derivative of this Schiff's base was prepared by the addition of an alcoholic solution of it to an aqueous solution of cobalt acetate. A tan material precipitated which was filtered, washed with water, and dried. It did not gain in weight when subjected to oxygen at 200 pounds pressure. The product was analyzed for nitrogen by a modified Kjeldahl procedure in which the digestion was begun with dilute sulfuric acid and

for cobalt by the ferricyanide titration method. Found: 5.92, 6.09 per cent nitrogen, 19.05, 19.15 per cent cobalt; calculated for  $C_{17}H_{16}O_2N_2Co$ : 8.25 per cent nitrogen, 17.4 per cent cobalt.

These analyses give a cobalt to nitrogen ratio of 3:2 rather than the desired 1:2, showing that the material prepared was not disalicylalttrimethylenediimine cobalt. Since the material did not carry oxygen no further attention was paid to it.

#### DISALICYLALTETRAMETHYLETHYLENEDIIMINE COBALT

Tetramethylethylenediamine was obtained from the Commercial Solvents Corporation as the free base in colorless, deliquescent crystals, melting gradually from  $86^{\circ}$ – $93^{\circ}$  (reported by Pirinskimi (8):  $97^{\circ}$ – $99^{\circ}$ ). Titration of a sample with standard hydrochloric acid indicated that the material contained 82.5 per cent tetramethylethylenediamine.

The Schiff's base disalicylaltetramethylethylenediimine formed readily on mixing alcohol solutions of two equivalents of salicylaldehyde and one equivalent of tetramethylethylenediamine. It was necessary to add a small amount of water to induce crystallization. The light yellow crystals were recrystallized from alcohol. Yield: 13.4 g., 41.6 per cent; m.p.:  $114.5^{\circ}$ . Found: 8.30, 8.35, 8.39 per cent nitrogen by the modified Kjeldahl method; calculated for  $C_{20}H_{24}O_2N_2$ : 8.64 per cent nitrogen.

Several preparations of the cobalt derivative of this Schiff's base were made in an effort to find conditions which would lead to a compound active toward oxygen. In one preparation 58.6 ml. of 1.087 N sodium hydroxide was added to 10.3 g. of disalicylaltetramethylenediimine and heated to  $60^{\circ}$  with 25 ml. of alcohol. A deep-red solution resulted which darkened as the heat was increased. One equivalent of cobalt chloride, 7.56 g. of  $CoCl_2 \cdot 6H_2O$ , in solution with 15 ml. of water and 10 drops of acetic acid, was added to this solution. After shaking, large lumps of light-brown material precipitated. This precipitate was washed with water and dried in air. Yield: 7.8 g., 62.7 per cent. On heating to  $170^{\circ}$  in vacuum the entire material became darker, and the edges showed evidences of charring. There was a weight loss of 17.1 per cent. It did not gain weight when subjected to oxygen at 200 pounds pressure.

In the next preparation the acetic acid was omitted, but the product was the same and again inactive. In a third preparation the effect of pH was studied more closely. A solution of the sodium salt of the Schiff's base in 25 per cent alcohol gave a reading of 11.6 using a glass electrode. This was reduced to 9.5 by the addition of acetic acid but it became necessary to add more alcohol to keep the material in solution. On the addition of an acid solution of cobalt chloride, pH 1.5, a light-brown precipitate formed which was filtered and washed with water. The black filtrate was nearly neutral, pH of 7.5. The brown product was definitely crystalline. After drying at  $155^{\circ}$  in a vacuum it failed to gain weight in oxygen at 180 pounds pressure.

In another preparation no alcohol or acid was used, and the sodium hydroxide was added in small amounts during digestion. Complete

solution did not occur owing to formation of some cobalt hydroxide. The final product was light red in color and was heated at several temperatures from 100° to 170° but was found to be inactive.

A further preparation was carried out by the pyridine method. To a mixture of 5 g. of tetramethylethylenediamine, 8.66 g. of salicylaldehyde, 8.41 g. (three equivalents) of pyridine, and 80 ml. of water, was added a solution of 8.60 g. of cobalt chloride in 20 ml. of water. The mixture was stirred vigorously and digested on a steam bath for 1 hour. A dark-red precipitate was obtained, which was filtered off, washed with water, and dried in air at 100°. Yield: 13.2 g., 96 per cent. The odor of pyridine was still apparent. On being heated at 140° in a vacuum this material lost 3 per cent in weight, and lost an additional 2.98 per cent at 170°. After each treatment it did not gain weight in oxygen at 200 pounds pressure.

All of the preparations mentioned above were analyzed for cobalt by decomposition with sulfuric acid followed by the ferricyanide titration. The values found for cobalt were within 0.5 per cent of the theoretical value of 15.47, indicating that the materials obtained were undoubtedly the cobalt compound expected.

#### DI-(2-HYDROXY-3-METHOXYBENZAL)-TETRAMETHYLETHYLENEDIIMINE COBALT

In this preparation 5 g. of tetramethylethylenediamine and 11 g. of 2-hydroxy-3-methoxybenzaldehyde were mixed in 30 ml. of alcohol. On shaking the mixture reaction suddenly occurred, a nearly solid mass being formed. The material was filtered and washed with a little water. Yield after air drying: 11 g., 70 per cent; m.p.: 182°. Loss on drying in air at 100°: 3.52 per cent.

To 3.78 g. of cobalt chloride,  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ , in 40 ml. of water was added 5.92 g. of di-(2-hydroxy-3-methoxybenzal)-tetramethylethylenediamine. As this mixture digested, one equivalent of sodium hydroxide as a 1 N solution was added slowly. A blood-red precipitate formed which was filtered off and washed with water. Yield after air drying: 7.7 g.; theoretical yield: 7.8 g. Loss on air drying at 105°: 7.16 per cent. When heated in a vacuum at 170° the sample decomposed. A second sample, carefully heated at 140°–155° in a vacuum, became slightly lighter in color and was cooled in a vacuum. Under oxygen at 200 pounds pressure, the original color completely returned, and the sample gained 0.38 per cent in weight.

A second preparation of the cobalt compound was carried out using a 50 per cent alcohol reaction medium, two equivalent of sodium hydroxide, and a temperature of 60° at the time of adding the cobalt chloride. The product was light brown in color, the yield was very low, and the material after vacuum drying at 150° did not gain weight in oxygen at 200 pounds pressure.

#### DI-(2-HYDROXY-3-NITROBENZAL)-TETRAMETHYLETHYLENEDIIMINE COBALT

2-Hydroxy-3-nitrobenzaldehyde, m.p.: 93°–95°, was dissolved in alcohol and treated with an alcoholic solution of the diamine. The result-

ing, bright-yellow Schiff's base was recrystallized from alcohol; m.p.: 181° with slight decomposition.

A quantity of 3 g. of di-(2-hydroxy-3-nitrobenzal)-tetramethylethylenediimine was dissolved in 13.35 ml. of 1.087 N sodium hydroxide containing 0.25 g. of sodium acetate, yielding a red solution upon slight heating. To this was added 1.73 g. of cobalt chloride dissolved in 35 ml. of boiling water and 0.3 ml. of acetic acid. The pasty reaction mass which resulted was filtered, washed with water, and dried at 100°. Yield: 3.20 g., 94 per cent. Samples of the material heated in vacuum at 150°, 170°, and 200° lost 4 to 6 per cent in weight but the products did not absorb oxygen on exposure to oxygen at 200 pounds pressure.

#### DISALICYLAL-2,3-BUTYLENEDIIMINE COBALT

2,3-Butylenediamine was prepared from the diacetate of dimethylglyoxime by the method of Balthis and Bailar (9). Although this method was found rather unsatisfactory a sufficient amount of the diamine was obtained to prepare a cobalt derivative.

A few crystals of cobalt acetate were dissolved in approximately 12 ml. water. Approximately 5 drops of the 2,3-butylenediamine was added. This solution was mixed with a solution of 5 drops of salicylaldehyde in absolute alcohol. A brilliant orange crystalline precipitate formed which was filtered off, washed with water, and dried in a vacuum at 100°. The product did not carry oxygen.

#### DISALICYLALHEXAMETHYLENEDIIMINE COBALT

Hexamethylenediamine was obtained from E. I. du Pont de Nemours & Co. as a white crystalline solid; m.p.: 31°–31.5°, reported by Coloniny (10): 30°. The Schiff's base was prepared in the usual manner by mixing one equivalent of the diamine with two equivalents of salicylaldehyde in warm absolute alcohol. On cooling, beautiful, bright crystals of disalicylalhexamethylenediimine, formed; m.p.: 68°–68.5° (from alcohol), 68.5° (from light petroleum ether). Found: 8.52, 8.21 per cent nitrogen, by the modified Kjeldahl method; calculated for  $C_{20}H_{24}O_2N_2$ : 8.65 per cent nitrogen.

The cobalt derivative was prepared by the addition of an alcohol solution of the Schiff's base to an aqueous solution of cobalt acetate, the quantities used being 9.72 g. of disalicylalhexamethylenediimine in 150 ml. of alcohol and 7.47 g. of cobalt acetate in 100 ml. of water. A black tar formed immediately, but within a few minutes this changed to a red crystalline mass which was filtered off and dried at 100° in a vacuum. This material did not gain weight when subjected to oxygen at 200 pounds pressure. Found: 14.20; 14.27 per cent cobalt; calculated for  $C_{20}H_{22}O_2N_2Co$ : 15.49 per cent cobalt.

In another preparation an aqueous solution of the sodium salt was prepared by treating a definite amount of sodium hydroxide with an

excess of disalicylalhexamethylenediimine, filtering off the excess, and then adding this solution to an aqueous solution of the required amount of cobalt chloride. The product was yellow green in color and inactive toward oxygen. Found: 15.95, 16.10 per cent cobalt; Calculated for  $C_{20}H_{22}O_2N_2Co$ : 15.49 per cent cobalt.

The direct simultaneous mixing of an alcohol solution of hexamethylenediamine, an aqueous solution of cobalt acetate, and salicylaldehyde all in the exact amounts required, with subsequent digestion at  $100^\circ$ , gave a red product which was also found to be inactive. Found: 14.50, 14.27, and 14.27 per cent cobalt; calculated for  $C_{20}H_{22}O_2N_2Co$ : 15.49 per cent cobalt.

#### DISALICYLALNONAMETHYLENEDIIMINE COBALT

Nonamethylenediamine was obtained from E. I. du Pont de Nemours & Company as a white crystalline solid; m.p.:  $35^\circ$ – $38^\circ$ ; reported by Colony (11):  $37^\circ$ – $37.5^\circ$ .

The condensation of nonamethylenediamine with two molecules of salicylaldehyde was easily effected in hot, absolute alcohol. The yellow crystalline Schiff's base was recrystallized from alcohol; m.p.:  $54.5^\circ$ – $55^\circ$ . It was also recrystallized from petroleum ether; m.p.:  $55^\circ$ .

The cobalt derivative was prepared by dissolving the Schiff's base in alcohol and adding the warm alcohol solution to a warm aqueous solution of cobalt acetate. Some tan precipitate formed but almost the entire amount of material was obtained as a brown tar. After drying, this product could be crushed to a powder and further dried. The powder did not absorb oxygen when subjected to oxygen at 200 pounds pressure.

#### DISALICYLALDECAMETHYLENEDIIMINE COBALT

Decamethylenediamine was obtained from E. I. du Pont de Nemours & Company as a white, crystalline solid; m.p.:  $61.5^\circ$ ; reported by Phookan and Krafft (12):  $61.5^\circ$ ; by Braun (13):  $60^\circ$ . A weighed sample of this material was dissolved in a hot, 25 per cent alcohol solution and titrated with standard acid using methyl red as indicator; the material was found to be 99 per cent decamethylenediamine.

The condensation of salicylaldehyde and decamethylenediamine proceeded immediately on mixing in absolute alcohol. On cooling in ice a beautiful, brilliant yellow, crystalline precipitate formed. This was filtered off, washed with water, and dried. M.p. after recrystallization from alcohol:  $65^\circ$ . Found: 6.64, 7.05, 7.10, 7.00, 6.91, 6.77 per cent nitrogen by the modified Kjeldahl method; calculated for  $C_{24}H_{32}O_2N_2$ : 7.37 per cent nitrogen; for the monohydrate  $C_{24}H_{32}O_2N_2 \cdot H_2O$ : 7.00 per cent nitrogen.

Disalicylaldecamethylenediimine was found to be very insoluble in dilute sodium hydroxide making it necessary to use alcohol in preparing the cobalt derivative. Disalicylaldecamethylenediimine cobalt was prepared by dissolving 3.80 g. of disalicylaldecamethylenediimine and 0.4 g.

of sodium hydroxide in absolute alcohol. An aqueous solution of 2.4 g. of cobalt chloride,  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ , was added to the above solution. Immediately a small amount of fine, tan precipitate formed and with further stirring, a tar also formed which collected on the stirring rod. The tar was dried in a vacuum at  $100^\circ$ ; it solidified and was brown in color. This material did not gain in weight on exposure to oxygen at 200 pounds pressure.

It was thought that possibly a crystalline cobalt derivative of disalicylaldecamethylenediimine could be obtained if the preparation were carried out in a very dilute solution. This was tried and a flocculent blue precipitate was obtained. Its appearance was much the same as that of nickel dimethylglyoxime except that it was blue in color. Upon filtering the mixture, so little material was collected that it was discarded and no further work was done along this line.

It has been shown that disalicylaethylenediimine cobalt can be prepared by warming an aqueous paste of an intimate mixture of disalicylaethylenediimine and cobalt acetate together. This method offered a possible way in which to prepare the cobalt derivative of disalicylaldecamethylenediimine. Disalicylaldecamethylenediimine and cobalt acetate were ground together until an intimate mixture was obtained. Water was added and a paste formed. On warming, a brown tar was formed which was dried, ground, and found to be inactive toward oxygen. No practical or successful method of preparing disalicylaldecamethylenediimine cobalt was found.

#### DISALICYLAL-O-PHENYLENEDIIMINE COBALT

A quantity of 12.2 g. (0.1 mole) of salicylaldehyde was dissolved in 25 ml. of 95 per cent ethyl alcohol, and to it was added 5.14 g. of *o*-phenylenediamine (0.05 mole) dissolved in 100 ml. of 95 per cent ethyl alcohol warmed to  $50^\circ$ . The reaction proceeded more slowly than in the case of the corresponding condensation of ethylenediamine with salicylaldehyde. The solution turned yellow immediately, an orange precipitate began to form in about 30 seconds, and the reaction was complete in a few minutes. The product was filtered off, washed with alcohol, and dried at  $110^\circ$ ; m.p.:  $155^\circ$ – $158^\circ$ . The material was found to be insoluble in ether, petroleum ether, and carbon tetrachloride. A mixture of benzene and petroleum ether was found to be the most suitable solvent for recrystallization; a mixture of the material and petroleum ether was heated to the boiling point, and benzene was added until all of the orange material had dissolved. The solution was filtered while hot and allowed to stand over night, after which the product was filtered off, washed with petroleum ether, and dried. Three such recrystallizations gave a product melting at  $163.5^\circ$ . A fourth recrystallization from benzene and petroleum ether specially purified for optical rotation work gave a pure product, melting sharply at  $165.5^\circ$ – $166^\circ$ ; m.p. reported (14):  $166^\circ$ .

A solution was prepared of 6 g. of disalicylal-*o*-phenylenediimine in 150 ml. of warm water containing 1.5 g. of sodium hydroxide and 1 g. of

sodium acetate. This solution of the sodium salt was added with stirring to a solution containing 4.56 g. of cobalt chloride in 25 ml. of water at 60°. A precipitate formed immediately which was at first an olive green color, but which turned brown in a few minutes. This precipitate was centrifuged and washed with cold water. Approximately one-half of the brown precipitate was dried at 100° under a vacuum for 4 hours. The remaining portion was dried at 170° under a vacuum for 3 hours.

The portion of material which was dried at 100° was powdered in a mortar and weighed samples placed in oxygen at 200 pounds pressure. An increase in weight amounting to 0.1 per cent, but no change in color was observed. Although the material was not noticeably hygroscopic, it is doubtful if the slight increase in weight was due to absorption of oxygen. Upon further drying at 100° this brown compound lost weight and turned a dark red color identical in appearance with the portion of the same preparation originally dried at 170°.

The material dried at 170° became dark red. It was powdered in a mortar and dried to constant weight at this temperature. This material also did not gain weight on exposure to oxygen at high pressure.

A second preparation of this cobalt compound, made using a 50 per cent alcohol reaction medium, was identical in appearance and also inactive.

#### PENTAERYTHRITYLTETRAMINE AND SALICYLALDEHYDE

Pentaerythrityltetramine,  $C(CH_2NH_2)_4$ , obtained from E. I. du Pont de Nemours & Co. as a light-yellow oil boiling 96°–98°/4 mm., was condensed in absolute alcohol with four molecules of salicylaldehyde. Condensation occurred readily, but the orange-colored, oily product could not be made to crystallize. A cobalt derivative was prepared from a solution of the oil in alcohol. An insoluble, dirty-yellow cobalt derivative was obtained. This material was filtered off, dried at 100°, and alternately tested for oxygen-carrying capacity and treated at successively higher temperatures in a vacuum with the object of possibly rendering it active. All tests were negative and it was concluded that the material merited no further consideration.

#### DIETHYLENETRIAMINE AND SALICYLALDEHYDE

Diethylenetriamine, obtained from the Carbide and Carbon Chemicals Corporation as a light-yellow liquid, was distilled and a fraction boiling 203°–205°/740 mm. taken for use. A sample of this amine was titrated with standard hydrochloric acid using methyl red as indicator; assuming the amine to be diacidic, the analysis gave a purity of 105 per cent, indicating probably that a portion of the imino group also reacted with the acid.

Two equivalents of salicylaldehyde and one of diethylenetriamine were condensed in alcohol. No precipitate formed, and on evaporation a yellow viscous oil was obtained which could not be induced to crystallize. A solution of 15.5 g. of this oil in hot alcohol was added to an aqueous



solution of 12.5 g. of cobalt acetate. No precipitate formed, and on evaporation a tar was obtained which was dried and ground, yielding a brown powder. This material gained about 1 per cent in weight on exposure to air probably owing to the absorption of moisture. It did not absorb oxygen.

Other preparations of this cobalt compound, made by mixing cobalt acetate, salicylaldehyde and diethylenetriamine in water in the correct proportions gave the same inactive product.

#### DIETHYLENETRIAMINE AND 2-HYDROXY-3-NITROBENZALDEHYDE

A solution of 8.4 g. of 2-hydroxy-3-nitrobenzaldehyde, m.p.:  $107^{\circ}$ – $108^{\circ}$ , in 200 ml. of 50 per cent alcohol was prepared. When solution was complete, a quantity of 2.5 g. of diethylenetriamine in 50 ml. of water was added. Upon cooling in ice, orange crystals separated which were filtered off, washed with water, and dried. Yield: 8.7 g.; m.p.:  $80^{\circ}$ – $81^{\circ}$ .

To 4.01 g. of di-(2-hydroxy-3-nitrobenzal)-diethylenetriamine dissolved in a solution of 0.8 g. of sodium hydroxide in 100 ml. of water was added 4.5 g. of cobalt chloride dissolved in 50 ml. of water. A fine precipitate formed which was filtered off and dried in a vacuum at  $100^{\circ}$ . This material was dark orange in color. Yield: 2 g. When heated at temperatures ranging from  $100^{\circ}$  to  $170^{\circ}$  and followed by treatment with oxygen at 200 pounds pressure, an increase in weight of about 0.2 per cent was observed. No characteristic change in color occurred, the increase in weight being undoubtedly due to the absorption of moisture.

#### DIETHYLENETRIAMINE AND 2-HYDROXY-5-NITROBENZALDEHYDE

To 16.8 g. of 2-hydroxy-5-nitrobenzaldehyde, m.p.:  $120^{\circ}$ – $121^{\circ}$ , dissolved in 200 ml. of alcohol and 100 ml. of water was added 5.2 g. of diethylenetriamine in 100 ml. of water. Upon cooling, fine yellow crystals separated which were filtered off and washed with water. These crystals were then dissolved in 200 ml. of water containing 4 g. of sodium hydroxide. To the hot solution was added a solution of 11.89 g. of cobalt chloride in 50 ml. of water. A fine, light brown precipitate formed instantly which was filtered off and dried at  $100^{\circ}$  in a vacuum. Yield: 9 g. When heated and subjected to oxygen under pressure there was no apparent change in color or significant gain in weight.

#### TRIETHYLENETETRAMINE AND SALICYLALDEHYDE

Triethylenetetramine, obtained from the Carbide and Carbon Chemicals Corporation as a yellow liquid, was used without further purification. The condensation of salicylaldehyde with triethylenetetramine was effected in a hot alcohol solution. The Schiff's base could not be isolated as a crystalline product but only as a viscous, yellow oil. An alcohol solution of this Schiff's base was added with vigorous agitation to an aqueous solution of one equivalent of cobalt acetate. On boiling away a portion of the solvent, the product was recovered as a black tar which was removed, dried, and ground to a powder. The product was inactive toward oxygen.

## TRIETHYLENETETRAMINE AND 2-HYDROXY-3-NITROBENZALDEHYDE

To 8.4 g. of 2-hydroxy-3-nitrobenzaldehyde dissolved in a solution of 100 ml. of alcohol and 50 ml. of water was added 3.6 g. of triethylenetetramine in 50 ml. of water. The solution became dark red, but even when cooled in ice no crystalline condensation product precipitated. After prolonged cooling a heavy dark red oil separated. The oil was separated, washed with water, and dried.

This Schiff's base in the form of a heavy oil was dissolved by adding the calculated equivalent of sodium hydroxide, assuming complete condensation to have taken place. To the hot solution was added the equivalent amount of cobalt chloride. A dark, turbid solution was obtained. After standing over night, a dark brown precipitate formed. This was filtered off and, although resembling other oxygen carriers in its purple color, it did not absorb oxygen.

## TRIETHYLENETETRAMINE AND 2-HYDROXY-5-NITROBENZALDEHYDE

To 16.7 g. of 2-hydroxy-5-nitrobenzaldehyde dissolved in 100 ml. of alcohol and 50 ml. of water was added 7.3 g. of triethylenetetramine in 50 ml. of water. Granular yellow crystals separated which were filtered off and dried. Yield: 9 g.; m.p.: above 220°. To 4.44 g. of di-(2-hydroxy-5-nitrobenzal)-triethylenetetramine dissolved in 150 ml. of water containing 0.8 g. of sodium hydroxide was added a solution of 4.53 g. of cobalt chloride in 50 ml. of water. A yellow-brown, rather granular precipitate formed instantly which was filtered off, and dried. It was heated at 150° in a vacuum and then subjected to oxygen at 200 pounds pressure. It did not gain in weight.

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# STUDIES ON OXYGEN-CARRYING COBALT COMPOUNDS

## X. COBALT DERIVATIVES OF THE SCHIFF'S BASES OF SALICYLALDEHYDE WITH ALKYLAMINES

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As shown in Paper IX of this series the cobalt derivatives of the Schiff's bases of salicylaldehyde with diamines other than ethylenediamine do not possess the property of absorbing oxygen. It was of interest to determine if the corresponding compounds using two equivalents of an alkylmonamine in place of ethylenediamine would be active toward oxygen.

In the case of the parent oxygen-carrying compound, bi-(disalicylal-ethylenediimine)- $\mu$ -aquo-dicobalt, it was only necessary to bring together, simultaneously, a cobalt salt, salicylaldehyde, and ethylenediamine, the formation of the Schiff's base and its cobalt derivative taking place together. This procedure failed with the alkylamines, the product being only cobalt disalicylaldehyde as indicated by the cobalt analysis and the absence of any amine in the product. By first preparing and isolating the Schiff's bases and then reacting an alcohol solution of the base with the cobalt salt it became possible to obtain the cobalt derivative. Even in this manner, however, the products were not always very pure. Evidently the Schiff's base underwent hydrolysis and the product in several cases contained some cobalt disalicylaldehyde. The latter, however, was usually sufficiently different in crystalline character and was precipitated after the other material had already formed so that a mechanical separation of the two was possible.

None of the disalicylalkylimine cobalt compounds prepared were active toward oxygen.

### EXPERIMENTAL WORK

#### THE SCHIFF'S BASES OF ALKYLAMINES AND SALICYLALDEHYDE

The Schiff's bases of the lower alkylamines with salicylaldehyde are high-boiling, yellow oils insoluble in water. They were made by reacting an excess of salicylaldehyde with excess amine. The amine was added to the aldehyde slowly and with vigorous stirring until an excess of amine was present as indicated by the white fume produced when hydrochloric acid was brought near the solution. A yellow oil was obtained, and considerable heat was evolved. After cooling, the oil was washed several times with water to remove the excess of amine. The washings were extracted with benzene, and the benzene extract was added to the main

portion of the oily product. This mixture was then distilled at atmospheric pressure, water and benzene distilling first followed by pure benzene. The Schiff's base was then finally distilled under vacuum.

TABLE I  
PROPERTIES OF SALICYLAMYLIMINES

Alkylamine	Boiling Range of Schiff's Base	Color	Yield (percentage)
Methylamine . . . . .	115°-117°/12 mm.	yellow	91
Ethylamine . . . . .	129°-133.5°/20 mm.	deep yellow	85
<i>n</i> -Propyl . . . . .	139.5°-142°/17 mm.	yellow	89
<i>iso</i> -Propyl . . . . .	130°-132°/17 mm.	yellow	81
<i>n</i> -Butyl . . . . .	150°-160°/20 mm.	reddish-yellow	91
<i>n</i> -Amyl . . . . .	155°-164°/15 mm.	reddish-yellow	81

#### DISALICYLAMMETHYLIMINE COBALT

To 0.1 mole of the Schiff's base, disalicylalmethylimine, dissolved in 50 ml. of absolute alcohol in a 3-necked, round bottom flask equipped with a mechanical stirrer and nitrogen inlet and outlet tubes, was added with constant stirring in a nitrogen atmosphere, a pulverized mixture of 0.05 mole of cobalt acetate and 0.1 mole of sodium bicarbonate. The stirring was continued until the evolution of carbon dioxide ceased. The flask was then heated and kept just below boiling for 15 minutes. Distilled water was then added to the dark solution until a tarry mass formed together with some dull, yellowish-green, solid precipitate. The latter was separated from the tar and solution, washed with distilled water, and dried in a vacuum at 70°. The cobalt in this material was determined by digesting a sample with nitric acid and sulfuric acid and followed by ignition and weighing as cobalt sulfate. Found: 18.5 per cent Co; theoretical for  $C_{10}H_{10}O_2N_2Co$ : 18.0 per cent Co.

#### DISALICYLALETHYLIMINE COBALT

This preparation was carried out using the same procedure employed above for the methyl compound. Two solid materials were obtained, brick-red lumps and fine, granular, yellowish-orange material. Both were dried in a vacuum at 70°. Found for the brick-red material: 15.0 per cent Co; found for the yellowish-orange material: 24.7 per cent Co. Theoretical for  $C_{18}H_{20}O_2N_2Co$ : 16.6 per cent Co. It is probable that the Schiff's base hydrolyzed partially and that the second material was largely cobalt disalicylaldehyde, the theoretical cobalt content of which is 19.6 per cent, contaminated by other cobalt-amine compounds.

#### DISALICYLAL-*n*-PROPYLIMINE COBALT

The same procedure was used. The orange-yellow product was dried in a vacuum at 80°. Found: 16.4 per cent Co; theoretical for  $C_{20}H_{24}O_2N_2Co$ : 15.4 per cent Co.

DISALICYLAL-*iso*-PROPYLIMINE COBALT

The same procedure was used. Red crystals separated from the solution during the reaction and it was not necessary to add water. Found: 15.88 per cent Co; theoretical for  $C_{20}H_{24}O_2N_2Co$ : 15.4 per cent Co.

DISALICYLAL-*n*-BUTYLIMINE COBALT

The same procedure was used. When water was added the solution gradually changed from dark brown to a milky yellow. A deep-red precipitate separated in the form of lumps followed by some finely divided orange-yellow material. These were separated from each other mechanically. Found for the red material: 13.17 per cent Co, for the orange-yellow: 17.0 per cent Co; theoretical for  $C_{22}H_{26}O_2N_2Co$ : 14.3 per cent Co. It is likely again that cobalt disalicylaldehyde was produced.

DISALICYLAL-*n*-AMYLIMINE COBALT

The same procedure was again used. On the addition of water two substances were thrown out of solution. The first was a semi-crystalline red mass and the other an orange-yellow powder. The former was probably the cobalt salt of the Schiff's base, but on drying in a vacuum it turned to a tar. The latter was probably cobalt disalicylaldehyde; found for it: 24.15 per cent Co.

## DISALICYLALANIL COBALT

The same procedure was used again employing the Schiff's base of salicylaldehyde with aniline. During the course of the reaction a red, crystalline product separated. These crystals were filtered, washed with water, and dried in a vacuum. Found: 14.55 per cent Co; theoretical for  $C_{26}H_{10}O_2N_2Co$ : 13.1 per cent Co.

\* \* \*

*Further discussions of the "Studies on Oxygen-Carrying Cobalt Compounds" will follow in subsequent issues of the Journal of Science.*

# STUDIES ON OXYGEN-CARRYING COBALT COMPOUNDS<sup>1</sup>

## XI. OXYGEN-CARRYING COMPOUNDS DERIVED FROM MIXTURES OF o-HYDROXYALDEHYDES

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Speculation as to the effect of preparing oxygen-carrying cobalt compounds of the type being reported in this series of papers from mixtures of *o*-hydroxyaldehydes which singly yielded oxygen-carrying compounds was prompted by the possibility of conserving those aldehydes which were expensive or unavailable. The study was devoted first to equimolecular mixtures of salicylaldehyde and 2-hydroxy-3-methoxybenzaldehyde, and later was extended to mixtures of salicylaldehyde and 2-hydroxy-3-ethoxybenzaldehyde, and of 2-hydroxy-3-methoxybenzaldehyde and 2-hydroxy-3-ethoxybenzaldehyde. The mixtures of the aldehydes were condensed with ethylenediamine and the cobalt derivatives of the products made. These cobalt compounds differed markedly from the cobalt derivatives of the pure aldehydes, principally in having their oxygen pressure-temperature equilibria shifted downward. Other properties, such as the deoxygenation temperature and activation temperature, were also lowered and the rate of oxygenation of the materials was found to differ from those of the compounds derived from the pure aldehydes.

It thus appeared that there was involved a phenomenon somewhat similar to the lowering of the melting point of a material by admixture with an impurity. Because of the great similarity of the component aldehydes, mixed crystal formation appear quite probable. On the other hand, the new materials might be pure individual compounds of the Schiff's bases in which one molecule of each of the different aldehydes was attached to the ethylenediamine radical. At any rate, a new field was being laid open for exploration and the conservation of expensive or unavailable aldehydes would obviously be secondary in importance to the convenience of securing an oxygen-carrier possessing any desired oxygenation-deoxygenation characteristics by simply varying the composition of the aldehyde mixture.

Of the various methods of preparing the cobalt oxygen-carrying compounds, that involving the prior formation and preferably the isolation of the Schiff's base of the aldehyde and ethylenediamine has given the best results (Papers II, VI, and VII). In the preliminary studies involving the mixed aldehydes, therefore, the Schiff's base was prepared by the

<sup>1</sup>Preceding parts of this discussion were published in this Journal as follows: Papers I, II, and III, Vol. XXI, pp. 271-309, 1947; Papers IV, V, VI, and VII, Vol. XXI, pp. 311-49, 1947; Papers VIII, IX, and X, Vol. XXII, pp. 91-128, 1947.

addition of ethylenediamine to an equimolecular mixture of aldehydes dissolved in hot alcohol and causing the Schiff's base to separate by cooling. Because of the low solubility in alcohol of the Schiff's bases of salicylaldehyde, 2-hydroxy-3-methoxybenzaldehyde and 2-hydroxy-3-ethoxybenzaldehyde, it was expected that the mass so obtained would be a mechanical mixture of the two Schiff's bases possibly containing also a mixed Schiff's base; that is, a base derived by the condensation of one molecule of ethylenediamine with one molecule each of the two aldehydes used. It was expected that the products would melt over a broad temperature range considerably below the melting points of the pure Schiff's bases; that is, disalicylaldehylenediimine:  $123^{\circ}$ , di-(2-hydroxy-3-methoxybenzal)-ethylenediimine:  $162\text{--}163^{\circ}$ , and di-(2-hydroxy-3-ethoxybenzal)-ethylenediimine:  $134\text{--}136^{\circ}$ .

The product derived from an equimolecular mixture of salicylaldehyde and 2-hydroxy-3-ethoxybenzaldehyde, however, melted fairly sharply at  $81\text{--}84^{\circ}$  and an identical melting point was obtained with a mixture prepared by grinding together equimolecular amounts of the two pure Schiff's bases. In the case of the mixture of salicylaldehyde and 2-hydroxy-3-methoxybenzaldehyde, the product melted over the range  $120\text{--}136^{\circ}$ . Mixed melting points of this product with the two pure Schiff's bases were  $120\text{--}142^{\circ}$  so that it appeared that the material obtained was a mixture of the two Schiff's bases. In the case of the equimolecular mixture of 2-hydroxy-3-methoxybenzaldehyde and 2-hydroxy-3-ethoxybenzaldehyde, yellow, needle-like crystals were obtained which melted at  $161\text{--}163^{\circ}$ , that is, had the same melting point as di-(2-hydroxy-3-methoxybenzal)-ethylenediimine, and further a mixed melting point of this product with di-(2-hydroxy-3-ethoxybenzal)-ethylenediimine gave  $118\text{--}135^{\circ}$ . This would indicate that the product was simply the pure methoxy Schiff's base. However, this could not be the case since the yield was 90 per cent and at least 40 per cent of the aldehyde present in the Schiff's base must have been the ethoxy aldehyde. This preparation was repeated and on this occasion the product resembled di-(2-hydroxy-3-ethoxybenzal)-ethylenediimine and melted over the range  $98\text{--}105^{\circ}$ . The mixed melting points of this product with di-(2-hydroxy-3-methoxybenzal)-ethylenediimine and di-(2-hydroxy-3-ethoxybenzal)-ethylenediimine were  $110\text{--}120^{\circ}$  and  $108\text{--}115^{\circ}$ , respectively.

It was evident from this work that in preparing the Schiff's bases in this manner, a great deal of uncertainty existed as to the nature of the product and that to make the cobalt compounds with such materials could only lead to inconsistent results.

None of the results just presented could be interpreted as evidence for the existence of a mixed Schiff's base. Indeed, as reported in Paper XII, attempts to make such an unsymmetric Schiff's base failed completely. It was proved that the double bond between the aldehyde carbon atom and the nitrogen atom is very labile, and that in alcohol the Schiff's base is in equilibrium with the aldehyde and ethylenediamine. In view of this it appeared impossible to predict just what the compositions of

the cobalt derivatives were going to be, and in order to secure reasonably uniform results the procedure for making the mixed aldehyde compound was standardized. A mixture of the proper weights of the pure Schiff's bases was dissolved in alcohol and the solution treated with a solution of cobalt chloride to precipitate the oxygen-carrying compound.

All of the materials prepared from mixtures of aldehydes became active toward oxygen at temperatures below the activation temperatures of the compounds from the pure aldehydes; for the most part the materials became active on drying at 100°. The oxygen-carrying capacities of the mixed materials were invariably below the expected, theoretical values, but in all cases were sufficiently high so that the materials could be used practically. The temperatures of deoxygenation were all lower than those of the end members of the series, this being most striking in the case of the series containing salicylaldehyde and 2-hydroxy-3-ethoxy-benzaldehyde. Several members of this series deoxygenated at temperatures in the range of 25° to 40°. The rates of oxygenation of the members of the three series varied markedly with composition, being for the most part faster than the end materials of the various series. Invariably the optimum temperature of oxygenation of these materials lay below 0°. Of the individual materials, that derived from a mixture of 90 mole per cent of 2-hydroxy-3-ethoxy-benzaldehyde and 10 mole per cent salicylaldehyde was of particular interest, being easily activated and very rapid in its action toward oxygen. This material absorbed oxygen at 0° as rapidly as 3-Methoxy Co-Ox and possessed the added advantage of being activated at a temperature of only 100°.

## EXPERIMENTAL WORK

### GENERAL METHODS EMPLOYED

A uniform procedure was employed for the preparation of all of the cobalt compounds used from mixtures of aldehydes and ethylenediamine. The pure Schiff's bases were prepared individually by the reaction of two moles of the aldehyde with one mole of ethylenediamine in alcohol. The bases were obtained as yellow, crystalline compounds, which were sufficiently pure for this work without recrystallization. The requisite quantities of the two Schiff's bases were dissolved in dilute sodium hydroxide, the volume of the solution being of the order of 1,500 ml. per 50 g. of Schiff's base. The bases usually dissolved without difficulty, although the process of dissolution was speeded by vigorous stirring and by the use of a slight excess of sodium hydroxide. The necessary amount of cobalt chloride dissolved in approximately 300 ml. of water was added to the hot solution of the Schiff's bases with vigorous stirring. After a few minutes stirring the precipitated material was centrifuged from the mother liquor and washed with a liter of hot water. The material was dried at 100°, then ground and tested for oxygen-carrying capacity by the usual gravimetric method (Paper XIII, *Method A*). Materials which were inactive after drying at 100° were subjected to 120° in a



vacuum for activation and then again tested for oxygen-carrying capacity. This process was repeated, using successively higher temperatures until the maximum capacity was found. This heat treatment was not carried above  $180^{\circ}$  since these materials began to decompose at about that temperature.

A preliminary determination of the temperature of deoxygenation was made by placing a small amount of the oxygenated material on the melting point block and noting the temperature at which the color changed from black to brown. A more precise temperature of deoxygenation was also obtained using the same apparatus used to determine the rate of oxy-

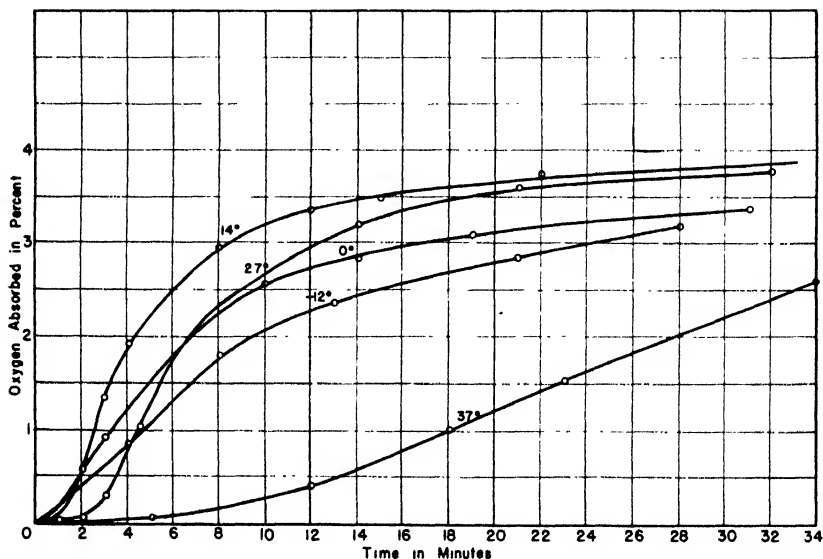


FIG. 1. Rate of oxygenation of Co-Ox in oxygen at 710 mm. pressure.

genation of the material (Paper XIII, *Method G*). A sample of completely oxygenated material in the reaction vessel of the rate apparatus was heated very slowly by heating the water in the bath surrounding the sample tube. The water bath was warmed and readings on the manometer taken at intervals of about twenty minutes. A total time of about two hours was taken for the experiment so that the sample and water bath were practically at thermal equilibrium at all times. The extent of deoxygenation was followed on the manometer in the same way that the extent of oxygenation was followed. The oxygen was not expelled suddenly at some particular temperature but was evolved gradually over a  $15^{\circ}$  interval.

The rate of oxygenation of these materials was determined using the Manometric Rate Apparatus described in Paper XIII of this series (*Method G*). The rates of oxygenation of Co-Ox, 3-Methoxy Co-Ox, and of 3-Ethoxy Co-Ox were also determined with the same apparatus so

that a comparison of all the materials could be made, Figures 1, 2, and 3. The copper sample tube described was used; twenty minutes was allowed for deoxygenation at  $100^{\circ}$  in a vacuum, and thirty minutes was allowed for cooling before oxygenation was begun. Samples of approximately 20 g. were used. The saturation values indicated by the rate apparatus were about 0.5 weight per cent below the true capacity of the compounds as

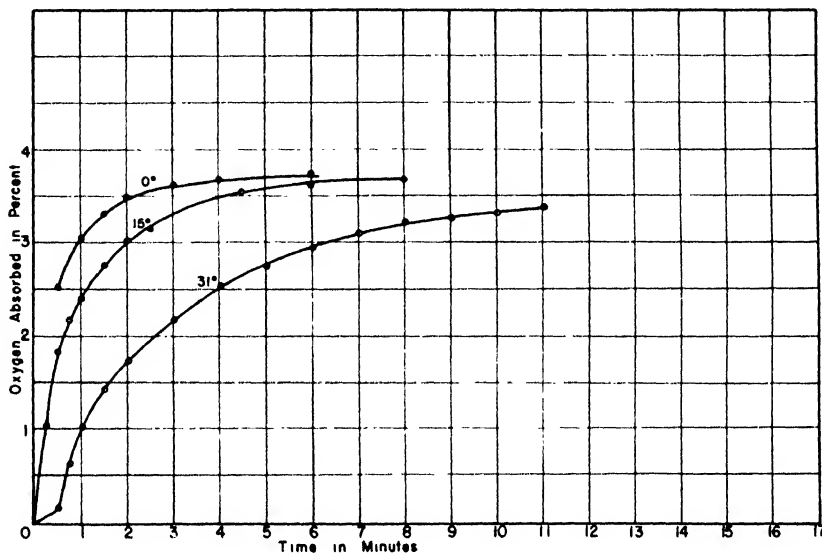


FIG. 2. Rate of oxygenation of 3-Methoxy Co-Ox in oxygen at 710 mm. pressure.

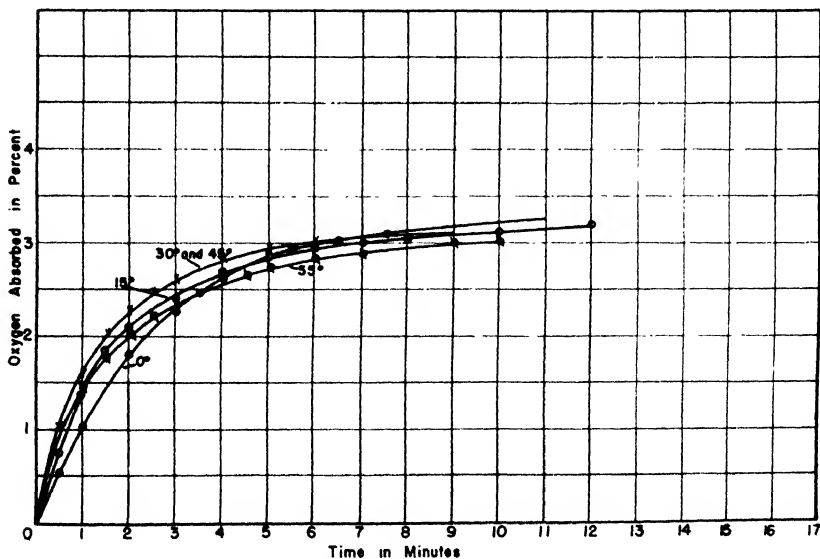


FIG. 3. Rate of oxygenation of 3-Ethoxy Co-Ox in oxygen at 710 mm. pressure.

determined gravimetrically. This is due to the fact that the calibration of the rate apparatus was made by a pressure-volume method rather than against a known compound. It is of no importance as far as the general shape of the rate curves is concerned but should be kept in mind when capacity is being considered. The capacities as determined gravimetrically are given in the accompanying tables. The optimum oxygenation temperature was obtained from curves plotting the time of half saturation against temperature.

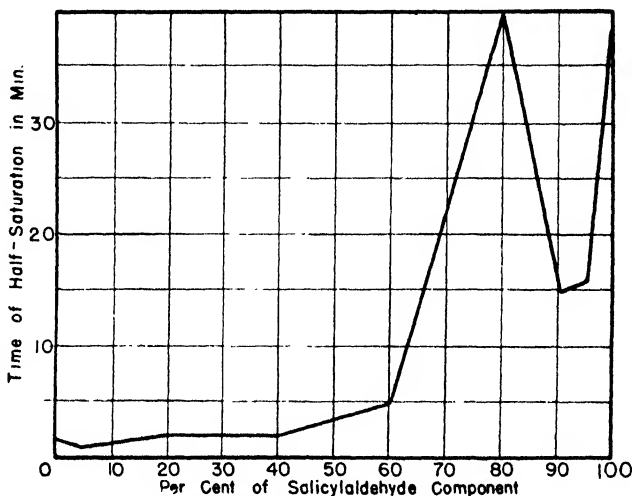


FIG. 4. Rate of oxygenation of cobalt materials derived from mixtures of salicylaldehyde and 2-hydroxy-3-methoxybenzaldehyde.

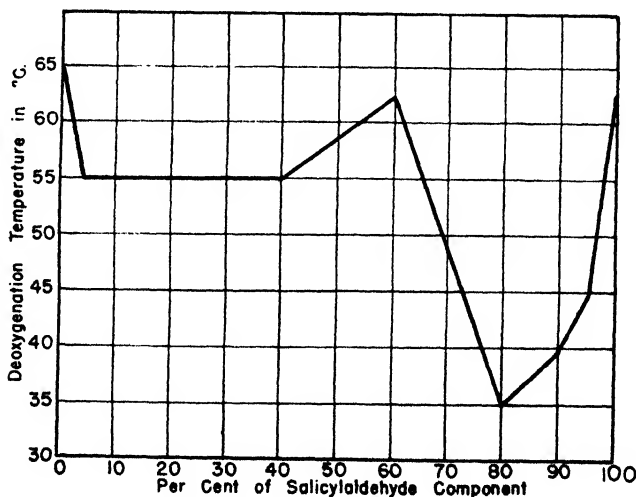


FIG. 5. Deoxygenation temperature of cobalt materials derived from mixtures of salicylaldehyde and 2-hydroxy-3-methoxybenzaldehyde.

## MATERIALS CONTAINING SALICYLALDEHYDE AND 2-HYDROXY-3-METHOXY-BENZALDEHYDE

The members of this series were prepared by the general method outlined above. Materials containing 95, 90, 80, 60, 40, 20, and 5 mole per cent of salicylaldehyde were prepared. The general shape of the rate curves was that of 3-Methoxy Co-Ox. Sufficient space is not available for the reproduction of all the data. The pertinent properties of these materials are summarized in Table 1 and in Figures 4 and 5.

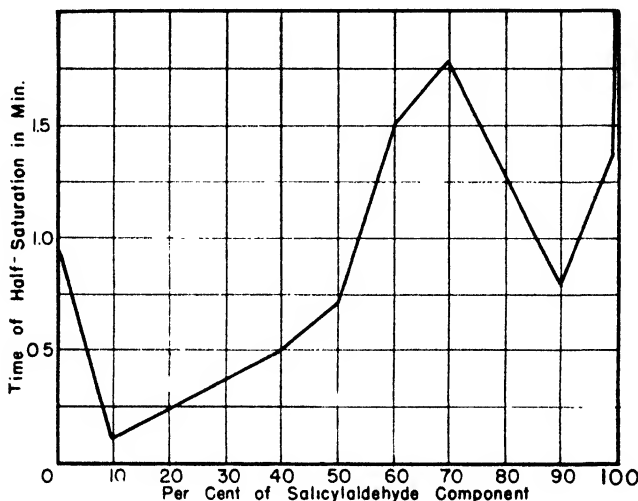


FIG. 6. Rate of oxygenation of cobalt materials derived from mixtures of salicylaldehyde and 2-hydroxy-3-ethoxybenzaldehyde.

The activation temperatures of these materials was uniformly lower than those of the pure end members of the series, Co-Ox and 3-Methoxy Co-Ox. The oxygen-carrying capacities of the materials were lower than the expected values. In some cases the capacities given in Table 1 were raised slightly by heating the materials to higher temperatures than those given as the activation temperature. This indicates possibly that these materials contained small amounts of pure 3-Methoxy Co-Ox in physical admixture.

The deoxygenation temperatures of these materials were all very low, in some cases only slightly above room temperature, and as would be expected the temperature of maximum rate of oxygenation was correspondingly low, below  $0^{\circ}$  in all cases. Many of the materials of this series were very fast, having about the same rate of oxygenation as the pure 3-Methoxy Co-Ox.

## MATERIALS CONTAINING SALICYLALDEHYDE AND 2-HYDROXY-3-ETHOXY-BENZALDEHYDE

Following the general procedure given above, a series of materials containing salicylaldehyde and 2-hydroxy-3-ethoxybenzaldehyde were

TABLE 1  
PROPERTIES OF THE OXYGEN CARRIERS PREPARED FROM MIXTURES OF DISALICYLAETHYLENEDIIMINE  
AND DI-(2-HYDROXY-3-METHOXYBENZAL)-ETHYLENEDIIMINE

Material (Mole Percentage of Disalicylaldehylenedimine in Mixture)	Activation Temperature (Centigrade)	Deoxygenation Temperature (Centigrade)	Optimum Oxygenation Temperature (Centigrade)	Time of Half-Saturation (Minutes)	Capacity (Percentage)
100 (Co-Ox).	100°	65°	15°	4.0 (15°)	4.70
95 ..	100°	45°	-10°	1.6 (-10°)	3.14
90 ..	100°	40°	-30°	1.5 (-16°)	3.07
80 ..	100°	35°	0°	4.1 (0°)	3.40
60 ..	120°	65°	-20°	0.5 (-16°)	2.75
40 ..	125°	55°	-15°	0.2 (-12°)	2.89
20 ..	130°	55°	-20°	0.2 (-17°)	3.58
5 ..	145°	55°	-15°	0.1 (-12°)	3.84
0 (3-Methoxy Co-Ox)	165°	75°	5°	0.16 (10°)	4.06

TABLE 2

PROPERTIES OF THE OXYGEN CARRIERS PREPARED FROM MIXTURES OF DISALICYLALETHYLENE-DIIMINE AND DI-(2-HYDROXY-3-ETHOXYBENZAL)-ETHYLENEDIIMINE

Material (Mole Percentage of Disalicylaethylenedimine)	Deoxygenation Temperature (Centigrade)	Optimum Oxygenation Temperature (Centigrade)	Time of Half- Saturation (Minute)	Capacity (Percentage)
100 (Co-Ox)	65°	15°	4.9 (15°)	4.8
90	40-44°	-30°	0.8 (-13°)	3.02
70	25-23°	-79°	1.8 (-79°)	
60	27-30°	-40°	1.5 (-12°)	
50	30-33°	-30°	0.7 (-10°)	
40	30-33°	-30°	0.5 (-15°)	
10	60-62°	-15°	0.1 (-14°)	3.27
0 (3-Ethoxy Co-Ox)	95°	30-40°	0.9 (30°)	3.7

prepared. The characteristics of these materials are summarized in Table 2, and Figures 6 and 7.

All of the members of this series became active on drying at temperatures below 100°. The capacity of several of the materials was not determined accurately because the compound deoxygenated rapidly at room temperature. However, in all cases the capacity was above 3 per cent. The rate at which all of the mixed materials of this series absorb oxygen is greater than that of the parent material, Co-Ox, and some are faster than the other end member of the series, 3-Ethoxy Co-Ox. The material containing 10 mole per cent of salicylaldehyde was exceptionally fast, oxygenating about as rapidly as 3-Methoxy Co-Ox. It could be used in a reversible cycle over the temperature range 0° to 60°. This material possesses the added advantage of being easily activated at 100°.

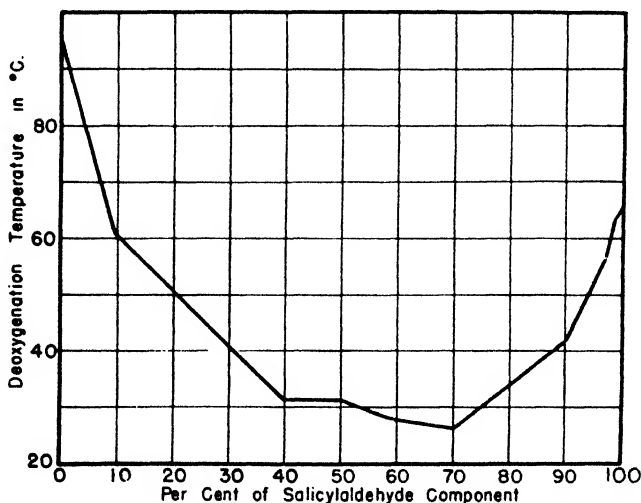


FIG. 7. Deoxygenation temperature of cobalt materials derived from mixtures of salicylaldehyde and 2-hydroxy-3-ethoxybenzaldehyde.

TABLE 3  
 PROPERTIES OF THE OXYGEN CARRIERS PREPARED FROM MIXTURES OF DI-(2-HYDROXY-3-METHOXYBENZAL)-ETHYLENEDIIMINE  
 AND DI-(2-HYDROXY-3-ETHOXYBENZAL)-ETHYLENEDIIMINE

Material (Mole Percentage of <i>di</i> -(2-hydroxy-3-ethoxybenzal) ethyleneimine)	Activation Temperature (Centigrade)	Optimum Oxygenation Temperature (Centigrade)	Deoxygenation Temperature (Centigrade)	Time of Half- Saturation at Optimum Temperature (Seconds)	Capacity (Percentage)
100 (3-Ethoxy Co-Ox) . . . . .	100°	40°	95°	37	3.80
90 . . . . .	100°	0°	70-75°	22 (at 3°)	3.76
70 . . . . .	100°*	0°	60-75°	14 (at 0°)	3.33
50 . . . . .	100°*	0°	60°	16 (at 0°)	3.76
30 . . . . .	100°*	-12°	50°	10 (at -12°)	3.70
10 . . . . .	125°	-10°	55-60°	8 (at -10°)	4.09
3 . . . . .	130°	-12°	55-60°	4 (at -12°)	4.01
0 (3-Methoxy Co-Ox) . . . . .	165°	5°	75°	10 (at 0°)	4.06

\* Not completely activated until heated to 170°.

## MATERIALS CONTAINING 2-HYDROXY-3-METHOXYBENZALDEHYDE AND 2-HYDROXY-3-ETHOXYBENZALDEHYDE

Following the general procedure given above a series of materials was prepared from mixtures of 2-hydroxy-3-ethoxybenzaldehyde, the mixtures taken having 90, 70, 50, 30, 10, and 3 mole per cent of 2-hydroxy-3-ethoxybenzaldehyde. The results are given in Table 3 and Figures 8 and 9. The temperature of activation of these materials decreased with

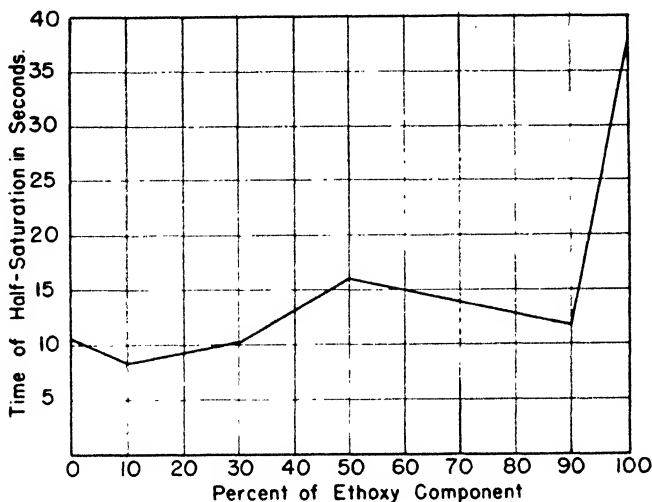


FIG. 8. Rate of oxygenation of cobalt materials derived from mixtures of 2-hydroxy-3-methoxybenzaldehyde and 2-hydroxy-3-ethoxybenzaldehyde.

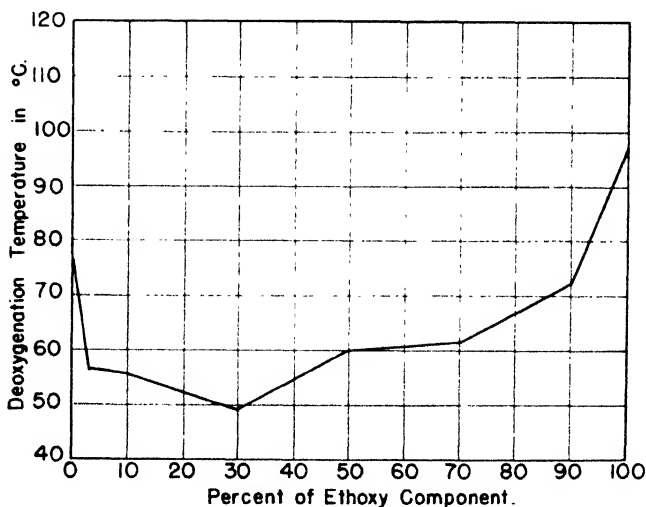


FIG. 9. Deoxygenation temperature of cobalt materials derived from mixtures of 2-hydroxy-3-methoxybenzaldehyde and 2-hydroxy-3-ethoxybenzaldehyde.



increasing amounts of 2-hydroxy-3-ethoxybenzaldehyde, being below  $100^{\circ}$  for those materials having 30 mole per cent and higher of the ethoxy component. The oxygen-carrying capacities of these materials were all somewhat below the theoretical values but in all cases were above 3.7 per cent. The rates of oxygenation of the materials were lower than that of 3-Ethoxy Co-Ox. The optimum temperature of oxygenation was found to be below  $0^{\circ}$  in each case. The temperature of deoxygenation in each case was lower than that of the pure compounds.

MATERIAL CONTAINING SALICYLALDEHYDE, 2-HYDROXY-3-METHOXY-  
BENZALDEHYDE, AND 2-HYDROXY-3-ETHOXYBENZALDEHYDE

By the general method outlined above, a material was prepared containing equimolecular amounts of salicylaldehyde, 2-hydroxy-3-methoxybenzaldehyde, and 2-hydroxy-3-ethoxybenzaldehyde. The brown material obtained was dried at  $105^{\circ}$  in a vacuum and found to carry 2.76 per cent oxygen. When heated to  $145^{\circ}$  for 1.5 hours in a vacuum it increased in activity to 3.28 per cent. The temperature of deoxygenation was found to be  $30-35^{\circ}$ . The rate of oxygenation of this material was determined at  $-18^{\circ}$ ,  $0^{\circ}$ , and  $18^{\circ}$ . The optimum temperature of oxygenation appeared to be about  $-20^{\circ}$ .

## STUDIES ON OXYGEN-CARRYING COBALT COMPOUNDS

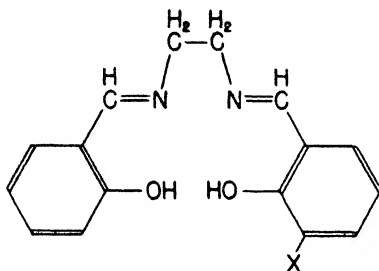
### XII. AN ATTEMPTED SYNTHESIS OF AN UNSYMMETRIC SCHIFF'S BASE OF ETHYLENEDIAMINE

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The interesting behavior of the oxygen carrier obtained by Diehl, Brouns, Harrison, and Liggett (Paper XI of this series), when a mixture of two aldehydes was condensed with ethylenediamine and the cobalt derivative of the product prepared, lead naturally to speculation as to the behavior of the cobalt derivative of a pure unsymmetric Schiff's base—that is, a base in which two different aldehydes are linked to the ethylenediamine molecule, as in the general formula



X being a substituent group.

It seems reasonable that two symmetrical and one unsymmetrical Schiff's bases might be expected to form when ethylenediamine was condensed with an equimolecular mixture of two aldehydes. The amount of each Schiff's base formed should depend on a number of factors. On the basis of two reasonable assumptions, the statistical probability is that 25 per cent of each of the symmetrical forms and 50 per cent of the unsymmetrical Schiff's base would be formed. The assumptions are first that the reaction takes place in a step-wise manner, rather than by a simultaneous condensation of the diamine with two aldehyde molecules, and second that the reaction rate is the same for the condensation of both aldehydes with the diamine.

On this basis it was thought that possibly by means of fractional crystallization, a separation of the three products might be accomplished. Careful fractional crystallization of the mixture of Schiff's bases obtained by the condensation of ethylenediamine with an equimolecular mixture of salicylaldehyde and 2-hydroxy-1-naphthaldehyde yielded only the two symmetric Schiff's bases, di-(2-hydroxy-1-naphthal)-ethylenediimine, and

disalicylaethylenediimine, the former being obtained first because of its lower solubility in alcohol. It is possible that some of the unsymmetric base was initially present in the intermediate crystal fractions, but repeated crystallization yielded only the two symmetric forms. A similar result was obtained on a mixture of salicylaldehyde and 2-hydroxy-3-nitrobenzaldehyde.

These results were inconclusive as far as the possible formation of an unsymmetric Schiff's base was concerned. It was further found that the addition of a half a mole of salicylaldehyde to a mole of ethylenediimine in alcohol led to the formation of a half mole of disalicylaethylenediimine, the unreacted ethylenediimine remaining in solution.

Apparently what was required was a method by which one aldehyde molecule was introduced at a time by having only one amino group present to react; the second amino group might be then introduced and the condensation with the second aldehyde effected. It was proposed to carry out such a synthesis by first making a Schiff's base of  $\beta$ -bromoethylamine, for example, with salicylaldehyde,  $C_6H_4(OH)CH=N-CH_2-CH_2-Br$ , then to replace the bromine with an amino group, and then to add the second, different aldehyde giving the unsymmetric Schiff's base.

Some difficulty was experienced in the initial preparation of  $\beta$ -bromoethylamine (as the hydrobromide) but a satisfactory method for its preparation was devised. This amine was condensed with salicylaldehyde and the Schiff's base salicylalbromethylimine obtained as a yellow crystalline material. In a similar manner  $\beta$ -bromoethylamine was condensed with 2-hydroxy-3-methoxybenzaldehyde, 2-hydroxy-3-ethoxybenzaldehyde, 2-hydroxy-3-nitrobenzaldehyde, and 2-hydroxy-1-naphthaldehyde, yielding in each case a yellow crystalline solid.

Attempts were made to convert these Schiff's bases to the corresponding amino compounds by reaction with ammonia under various conditions. The reactions were carried out using aqueous ammonia, ammonia under pressure, anhydrous liquid ammonia, and liquid ammonia in ether. In every case it was found that the bromine was replaced as desired but that the compound isolated was the symmetric Schiff's base.

It was concluded from these results that the double bond linkage between the aldehyde carbon atom and the nitrogen was very readily hydrolyzed in solution, and that continual rearrangement of the aldehyde attached to the amine was taking place. This would account for the failure to obtain an unsymmetric Schiff's base in our earlier fractional crystallization experiments.

In order to confirm further that hydrolysis of the Schiff's base was occurring, disalicylaethylenediimine dissolved in alcohol was treated with 2-hydroxy-1-naphthaldehyde and the mixture warmed for a short time. Di-(2-hydroxy-1-naphthal)-ethylenediimine was formed confirming the labile character of the carbon-nitrogen double bond.

Some thought was given the possibility of using the Gabriel synthesis to replace the bromine by an amino group in the Schiff's bases of  $\beta$ -bromo-

ethylamine. Since it had been shown that these Schiff's bases were readily hydrolyzed, it was obvious that the usual methods for decomposing the phthalimide intermediate would be impossible. Hydrazine hydrate has been used successfully in this connection on several compounds which were sensitive to the hydrobromic acid hydrolysis usually employed to split off the phthalic acid residue. Preliminary experiments in which hydrazine hydrate and disalicylaethylenediimine were brought together yielded disalicylazine, undoubtedly again because of hydrolysis of the disalicylaethylenediimine. It is certain as a result of these experiments that an unsymmetrical Schiff's base cannot be prepared in the presence of water and if formed under other conditions would not be stable when later brought into an aqueous solution.

### EXPERIMENTAL WORK

#### FRACTIONAL CRYSTALLIZATION OF THE MIXTURE OF SCHIFF'S BASES OBTAINED BY THE CONDENSATION OF ETHYLENEDIAMINE AND AN EQUIMOLECULAR MIXTURE OF SALICYLALDEHYDE AND 2-HYDROXY-1-NAPHTHALDEHYDE

A mixture of 20 g. of 2-hydroxy-1-naphthaldehyde and 11 g. of salicylaldehyde was dissolved in 250 ml. of absolute alcohol, and the solution warmed to 75°. To this, a solution containing 12 g. of ethylenediamine in 50 ml. of water was added slowly with vigorous stirring. The mixture was stirred for about one minute and then filtered immediately. The filtration was carried out at 65°, and after washing with a small amount of alcohol the condensation product was dried. The material melted above 280°, and was therefore nearly pure di-(2-hydroxy-1-naphthal)-ethylenediimine.

The filtrate was allowed to cool slowly to 35°, and a second crop of yellow crystalline material was filtered and washed with a little alcohol; m.p.: 122–200°. An attempt was made to recrystallize this material from absolute alcohol, but a lemon yellow precipitate formed, which would not dissolve; m.p.: above 300°. It is certain that this material was formed in the recrystallization process since the solution previously had been perfectly clear. The filtrate yielded crystals of disalicylaethylenediimine; m.p.: 123°, upon standing for two days.

The filtrate from the crop of crystals filtered at 35° was cooled slowly to 0° and then filtered. The crystalline compound from this fraction, m.p.: 140–180°, was warmed with 250 ml. of alcohol at 40° and filtered. An insoluble material, m.p.: 240–280°, was obtained. From the filtrate, pure disalicylaethylenediimine, m.p.: 124°, was obtained.

It seems very probable that some unsymmetric Schiff's base was present in the intermediate crystal fractions, but upon recrystallization only the two symmetric forms were isolated.

Similar results were obtained working with the condensation product of ethylenediamine and an equimolecular mixture of salicylaldehyde and 2-hydroxy-3-nitrobenzaldehyde.

$\beta$ -BROMETHYLAMINE HYDROBROMIDE

This material has been prepared by the hydrolysis of  $\beta$ -bromethylphthalimide in a mixture of hydrobromic acid and acetic acid in a sealed tube (1). Although  $\beta$ -bromethylphthalimide may be readily prepared (2), the hydrolysis of the compound by a sealed tube reaction did not appear desirable in view of the fairly large quantity of compound desired. Gabriel also suggested that  $\beta$ -bromethylamine could be prepared by treating ethanolamine in a sealed tube with hydrobromic acid. This method appeared advantageous since ethanolamine is a relatively inexpensive and easily obtained starting material. It was thought possible to avoid the sealed tube reaction by employing anhydrous hydrogen bromide instead of aqueous hydrobromic acid. An attempt to prepare  $\beta$ -bromethylamine by this method failed and only a tarry residue resulted upon distillation of the reaction mixture under reduced pressure.

Another method for the preparation of  $\beta$ -bromethylamine has been described by Leffler and Adams (3). This method involves the preparation of ethanolamine hydrobromide followed by reaction with phosphorous tribromide, and subsequent isolation and purification of the  $\beta$ -bromethylamine hydrobromide. A yield of 72 per cent was reported.

The method described by Leffler and Adams was closely followed, but all attempts to isolate the pure  $\beta$ -bromethylamine hydrobromide from the final reaction product failed. It was obvious that several rather important precautions and details had been omitted from the procedure described. The preparation was repeated using smaller quantities and close attention was given to several possible sources of difficulty. This preparation proved entirely successful and the desired product was obtained in pure form and in excellent yield. The procedure was as follows:

In a 1-l. wide mouth, round bottom flask fitted for vacuum distillation with a Claisen head, condenser and receiver, were placed 244 g. (4 moles) of ethanolamine (b.p.: 165–167°/736 mm.) and 690 g. (4.1 moles) of 48 per cent hydrobromic acid. The mixture was heated by a water bath maintained at 90–100° while the water and excess hydrobromic acid were removed by distillation at 10–20 mm. pressure. The last of the water distilled rather slowly and the heating was continued for thirty minutes after the water first appeared to have been all removed. The moisture which collected in the upper part of the flask and the Claisen head was removed by cautiously applying heat directly to this part of the apparatus. The presence of any residual water was found to be very detrimental, causing the final product to be gummy and difficult to remove from the flask. The reaction mixture was then allowed to cool whereupon it crystallized as a dry, nearly white, crystalline solid.

The flask was then fitted with a water cooled reflux condenser, and to the ethanolamine hydrobromide in the flask was added 550 g. (2.05 moles) of phosphorus tribromide. The flask was heated cautiously with a burner and the reaction mixture was shaken frequently. Upon heating,

the reactants gradually melted and the phosphorus tribromide settled to the bottom of the flask while the ethanolamine hydrobromide formed a dark brown upper layer. The heating was continued gently for about twelve minutes with frequent agitation; the mixture gradually began to boil more vigorously, turned brilliant orange in color, and became thick. It was found that the reaction mixture with phosphorus tribromide should not be heated more than necessary at any time during the reaction. If the mixture was fused by heating strongly, it was almost impossible to remove the solid from the reaction vessel. If the mixture was not heated excessively a crumbly, granular mass, easily removed from the reaction vessel, was obtained. The time required after the addition of the phosphorus tribromide was about twenty minutes.

The top of the condenser was then connected to a 250 ml. suction flask by means of glass tubing and the suction flask attached to a water aspirator. The water was drained from the condenser to hasten the removal of the volatile products. A considerable volume of white fumes was evolved and the volatile materials present in the mixture were distilled off by the application of a very little heat. Toward the end of the reaction the mixture became a very thick paste. The flask and contents were allowed to cool to room temperature under vacuum and then air was admitted slowly to the flask. Occasionally as the air entered a blue flame was observed traveling down through the condenser into the flask, owing to the combustion of some gaseous reaction product present. The orange solid was removed with the aid of a metal spatula, washed with 800 ml. of dry ether, then placed in a large mortar, pulverized, and washed again with about 700 ml. of dry ether.

The material was then placed in a 4-l. beaker, and a mixture of 2,400 ml. of absolute alcohol and 800 ml. of anhydrous ethyl acetate added. Upon warming to boiling on the steam plate, nearly all of the orange solid dissolved. The solution was allowed to cool to room temperature and filtered. About 6 g. of reddish, amorphous material remained on the filter. The slightly turbid filtrate was then treated with 10 g. of activated charcoal. After approximately thirty minutes the solution was cooled a little and the charcoal filtered off.

The solvent was removed from the filtrate by distillation under slightly diminished pressure until about 400 ml. of liquid remained and a few crystals were observed on the cooler portions of the flask. Upon further cooling the entire mixture turned to a semi-solid, crystalline mass. The crystals were filtered on a Buchner funnel and then dried in air at 100°; m.p.: 170°; yield: 665 g. or 81 per cent. The material was recrystallized from anhydrous ethyl alcohol-ethyl acetate mixture as described above, white plates being obtained; m.p.: 172–173.5°.

$\beta$ -Bromethylamine hydrobromide is very soluble in absolute alcohol, about 85 g. per 100 ml. For this reason the solvent consisting of three parts of alcohol and one part of ethyl acetate is more satisfactory than alcohol alone.

ATTEMPTED ISOLATION OF THE FREE BASE,  $\beta$ -BROMETHYLAMINE

Two attempts were made to isolate the free amine from  $\beta$ -bromethylamine hydrobromide as follows: A quantity of 21.5 g. (0.1 mole) of  $\beta$ -bromethylamine hydrobromide was dissolved in 50 ml. of water and cooled in an ice bath to 0°. About 5 g. of sodium hydroxide was dissolved in 10 ml. of water and also cooled in an ice bath. The sodium hydroxide solution was added slowly with stirring to the ice cold, aqueous solution of  $\beta$ -bromethylamine hydrobromide. An amine odor was apparent immediately. The cold solution was immediately extracted with two 25 ml. portions of cold ether. The ether layer was separated and the ether removed by distillation under diminished pressure, using a water aspirator. A little yellow oil, which had the strong odor of an amine, remained in the flask. Upon warming very slightly, hardly to room temperature, the liquid suddenly began to boil vigorously, the reaction being complete in about thirty seconds. The remaining liquid was rather viscous and no longer had the odor of an amine. It did not form a Schiff's base with salicylaldehyde.

The decomposition of  $\beta$ -bromethylamine is undoubtedly a bimolecular condensation yielding piperazine hydrobromide. No further attempt was made to isolate the free amine as this step was found unnecessary for the preparation of the Schiff's bases.

SALICYLAL- $\beta$ -BROMETHYLIMINE

A solution of 108 g. (0.5 mole) of bromethylamine hydrobromide in 200 ml. of water was added to a solution of 61 g. (0.5 mole) of salicylaldehyde in 200 ml. of 95 per cent alcohol. The resulting solution was warmed to about 50° and to it was added slowly, with stirring, a solution containing 22 g. of sodium hydroxide in 20 ml. of water. The solution turned yellow and a heavy oily layer formed. Upon cooling, yellow crystals separated and the oily layer also solidified. The solid material was filtered and then recrystallized from 95 per cent alcohol; yield: 90 g., 70 per cent. A small amount of the yellow crystalline material was recrystallized three times from absolute alcohol; m.p.: 56–56.5°; reported (4): 56–57°.

2-HYDROXY-3-METHOXYBENZAL- $\beta$ -BROMETHYLIMINE

This preparation was carried out in the same manner as given above for the salicylaldehyde compound; m.p.: 73.5° (from absolute alcohol).

2-HYDROXY-3-ETHOXYBENZAL- $\beta$ -BROMETHYLIMINE

Same procedure; m.p.: 66.5° (from absolute alcohol).

2-HYDROXY-3-NITROBENZAL- $\beta$ -BROMETHYLIMINE

The 2-hydroxy-3-nitrobenzaldehyde used was carefully purified by slow crystallization from alcohol; m.p.: 110°. The procedure used above

was followed for the preparation of the Schiff's base; m.p.: 119–120° (from 50 per cent alcohol).

#### 2-HYDROXY-1-NAPHTHAL- $\beta$ -BROMETHYLIMINE

Same procedure; m.p.: 117°.

#### ACTION OF AQUEOUS AMMONIA ON SCHIFF'S BASES OF $\beta$ -BROMETHYLAMINE

A quantity of 2.5 g. of salicylal- $\beta$ -bromethylamine was pulverized in a mortar and then placed in a beaker with 50 ml. of aqueous ammonia. The beaker was cooled in an ice bath and a stream of ammonia gas passed into the mixture for fifteen minutes. The cold mixture was transferred to a Coca-Cola bottle which also had been cooled in an ice bath. The bottle was closed with a rubber stopper which was wired securely in place, wrapped in several towels, and then heated gradually to 100° in a steam bath. At the end of four hours the bottle was cooled gradually to room temperature, then placed in an ice bath for several minutes before opening. An orange solid had crystallized in the bottom of the bottle. This solid material was recrystallized from absolute alcohol; m.p.: 120–123°. A mixed melting point with pure disalicylalethylenediimine was found to be 120–123°. It was therefore concluded that this compound was disalicylalethylenediimine.

A repetition of this experiment in which a 50 per cent alcohol-water mixture was used as solvent gave the same product.

Similarly, with 2-hydroxy-3-ethoxybenzal- $\beta$ -bromethylimine there was obtained yellow, crystalline material, m.p.: 137–138.5°, which was proved by mixed melting point with a known sample to be di-(2-hydroxy-3-ethoxybenzal)-ethylenediimine.

#### ACTION OF AMMONIA ON DISALICYLAETHYLENEDIIMINE

Disalicylalethylenediimine was dissolved in dilute alcohol and treated with ammonia under the conditions described above. The original compound was recovered and no evidence was obtained of the formation of any hydrosalicylamide, the compound resulting from the condensation of three molecules of salicylaldehyde and two of ammonia.

#### ACTION OF AQUEOUS AMMONIA ON 2-HYDROXY-3-METHOXYBENZAL- $\beta$ -BROMETHYLIMINE

In order to determine if a temperature of 100° and ammonia under pressure were essential for the hydrolysis and amination reaction reported above, 2-hydroxy-3-methoxybenzal- $\beta$ -bromethylimine was dissolved in 50 per cent alcohol, saturated with ammonia at room temperature and then the solution heated to boiling. Upon cooling, orange crystals formed which were filtered, washed with alcohol, and dried; m.p.: 160°. It was therefore obvious that heating for a short period with aqueous ammonia was sufficient and that the conditions used above were far more drastic than necessary.



ACTION OF LIQUID AMMONIA ON 2-HYDROXY-3-METHOXYBENZAL- $\beta$ -BROMETHYLIMINE

It was found that liquid ammonia and 2-hydroxy-3-methoxybenzal- $\beta$ -bromethylimine did not react when mixed and warmed, allowing the ammonia to evaporate.

In another experiment an ether solution of the Schiff's base 2-hydroxy-3-methoxybenzaethylenediimine was treated with liquid ammonia. After the ammonia had evaporated and the ether solution warmed to room temperature, most of the ether was removed by distilling under diminished pressure. The compound was filtered and washed with ether; m.p.: 68–69°. It was recrystallized from anhydrous ether; m.p.: 70°. It appeared that the original Schiff's base had been recovered.

In another experiment about 5 g. of 2-hydroxy-3-methoxybenzal- $\beta$ -bromethylimine was dissolved in 50 ml. of anhydrous ether. The solution was placed in a large test tube and cooled by placing in a Dewar flask containing liquid ammonia. When the solution had reached the liquid ammonia temperature, about 25 ml. of liquid ammonia was added to the ether solution and the tube again placed in the Dewar flask. After forty-eight hours the crystalline material in the test tube was removed and washed with ether; m.p.: 149–152°. Upon recrystallization the m.p. was 160°, and a mixed melting point with pure di-(2-hydroxy-3-methoxybenzal)-ethylenediimine was 159–160°. The results of this last experiment are in contrast with those of the first two in which liquid ammonia was employed. Perhaps this was caused by moisture collected by condensation from the air, and also by the longer period of time during which the reaction took place.

## THE REACTION OF 2-HYDROXY-1-NAPHTHALDEHYDE AND DISALICYLAETHYLENEDIIMINE

About 5 g. of disalicylaethylenediimine was dissolved in 100 ml. of alcohol and warmed to boiling. To this hot alcohol solution was added about 2 g. of 2-hydroxy-1-naphthaldehyde dissolved in a little alcohol. Upon warming the resulting solution for a few minutes, a yellow crystalline material began to precipitate. Within three minutes a heavy precipitate had formed which was filtered off, washed with alcohol and dried; m.p.: above 300°. This compound was therefore di-(2-hydroxy-1-naphthal)-ethylenediimine. The reaction may be readily explained on the basis of hydrolysis of the disalicylaethylenediimine and the condensation of the amine with  $\beta$ -hydroxynaphthaldehyde. The reaction apparently goes to completion because the Schiff's base di-(2-hydroxy-1-naphthal)-ethylenediimine is very insoluble and apparently not readily hydrolyzed.

THE REACTION OF HYDROSALICYLAMIDE WITH 2-HYDROXY-3-NITROBENZAL- $\beta$ -BROMETHYLIMINE

Hydrosalicylamide was prepared by adding aqueous ammonia to an ether solution of salicylaldehyde. The resulting light yellow crystalline material was filtered, reslurried with absolute ether, filtered, and dried; m.p.: 158°, reported (5): 160°.

A quantity of 10 g. of hydrosalicylamide, 10 g. of 2-hydroxy-3-nitrobenzal- $\beta$ -bromethylimine, and 75 ml. of alcohol were placed in a Coca-Cola bottle, sealed and then heated to 100° in a steam bath for two hours. Upon cooling and opening a red crystalline material had separated. This material was filtered and washed with alcohol; m.p.: 205°. This compound was pulverized in a mortar, washed with hot alcohol, and filtered; m.p.: 245°. This indicated that di-(2-hydroxy-3-nitrobenzal)-ethylenediimine was formed. From the original filtrate a small amount of disalicylaethylenediimine was obtained; m.p.: 124°.

#### THE REACTION BETWEEN HYDRAZINE HYDRATE AND DISALICYLAETHYLENEDIIMINE

In a 200 ml. round bottom flask, 11.4 g. (0.05 moles) of salicylal- $\beta$ -bromethylimine was dissolved in 100 ml. of alcohol and 3.8 g. (0.1 moles) of 42 per cent hydrazine hydrate added. The solution was warmed slightly; a reaction seemed to commence even before the solution was heated to boiling. A few yellow crystals separated from the clear solution. A few of these were removed and washed with a little alcohol; m.p.: 205°. The mixture was refluxed gently for thirty minutes, during which more yellow crystalline material separated. The mixture was cooled and the crystals filtered. A portion of these crystals were recrystallized from absolute alcohol; m.p.: 216–217°. This compound was undoubtedly disalicylalazine; reported for this material: 213–214° (6).

A sample of disalicylalazine was prepared by the addition of hydrazine hydrate to a warm alcohol solution of salicylaldehyde. The condensation product was filtered and recrystallized twice from 50 per cent alcohol; m.p.: 216°. Probably the melting point reported in the above reference was 2° low. The melting point apparatus was calibrated at 212° and would therefore be correct within a fraction of one degree at 216°.

A mixed melting point of disalicylalazine and the compound from the above experiment indicated the compounds to be identical.

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# STUDIES ON OXYGEN-CARRYING COBALT COMPOUNDS

## XIII. APPARATUS FOR DETERMINING THE CAPACITY AND RATE OF OXYGENATION OF SOLID MATERIALS

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Given a compound which has the unique property of functioning as an oxygen-carrier, the questions arise immediately: how much oxygen does it absorb, and, how rapidly does it do so? The answer to the first question can be obtained without much difficulty, even in those cases in which the oxygen-carrier tends to gain or lose its oxygen rapidly or in which it is hygroscopic and will not admit of exposure to the atmosphere during weighing. The second question is not so easily answered. The rate of oxygenation depends on whether air or oxygen is used, on the temperature and pressure, and on the rate of heat transfer and hence on the constructional features of the rate apparatus.

The simplest method of determining the oxygen-carrying capacity of a solid material is by placing a boat bearing a weighed quantity of material in an atmosphere of oxygen at a suitable pressure, then after a sufficient time removing and weighing the boat and oxygenated material. The details of carrying this out are described here under *Method A, The Direct Gravimetric Method*. If the oxygenated compound loses its oxygen rapidly when the pressure is released or if it is hygroscopic and weighing in the normal fashion cannot be relied upon, then the oxygen may be expelled and collected and its volume measured (*Method B, The Gas Evolution-Nitrometer Apparatus*), or advantage may be taken of the change in pressure of the system during the oxygen absorption (*Method C, Differential Manometric Apparatus*). The latter method can be used also over a wide range of temperature.

From the standpoint of manufacturing oxygen, the rate at which oxygen is taken from air is of more interest than the rate from an atmosphere of oxygen. The rate of oxygenation in air, however, is influenced by the rate at which the air is passed over the solid material, since it is obvious that the nitrogen left after the removal of the oxygen stops the oxygenation process. In addition, considerable heat is evolved in the oxygenation reaction and this heat would be partially carried away by the air. The thermal conductivity of the container and of the support, and the thickness of the bed of the material play a part.

For engineering purposes or for securing the information required for postulating chemical mechanisms to explain the absorption of oxygen, the effects of temperature and pressure on the oxygenation rate must be

determined, and such information can more easily be secured using pure oxygen than using air. When oxygen is used it is not necessary that the gas be circulated over the bed of material, but it is essential that the oxygen be of high purity since otherwise the accumulation of nitrogen about the material would stop the oxygenation.

It would appear that the rate of oxygenation in oxygen should be five times greater than the rate in air at the same pressure. This point has not been checked and may not necessarily be true, owing to the accumulation of nitrogen within the particles of the oxygen-carrying material as oxygen is removed from the air. Gas diffusion must be one of the principal controlling factors in this situation, and until more has been learned about the mechanism of the oxygenation-deoxygenation process, it seems best to carry out the rate studies with air where necessary and with oxygen where the nature of the results desired permit the convenience of using oxygen.

In the interests of conserving time, the apparatus should be one which gives the complete oxygenation curve at one experiment, rather than an apparatus in which points on the curve are obtained as a result of a series of oxygenations discontinued after different intervals of time. *Method D, Gravimetric Rate Method*, in which the rate of oxygenation is followed by weighing the sample, falls in this category and therefore is less acceptable than methods in which the rate of oxygenation is followed continuously by the change in some property of the system, such as the gas pressure, the volume, or the magnetic susceptibility.

*Method D, The Gravimetric Rate Method*, was poorly adapted to the determination of the rate of oxygenation at various temperatures and pressures. *Method E, The First Gas Volumetric Method*, in which the volume of oxygen absorbed was measured, was better in this respect. With it the rate of oxygenation of Co-Ox was measured at temperatures from  $-7^{\circ}$  to  $40^{\circ}$  and at pressures from 200 mm. to 870 mm. of mercury. Unfortunately it employed water as a retaining liquid and delivered oxygen saturated with moisture, a fatal defect in the case of the 3-alkoxy derivatives which are extremely hygroscopic. A *Second Gas Volumetric Method, Method F*, was designed to furnish dry oxygen and was considerably simpler in operation than *Apparatus E*.

The heat of oxygenation of the compounds of the Co-Ox type is about 20,000 calories per mole of oxygen. The shape of the rate curve is greatly altered when this heat is not removed rapidly. In the *Differential Manometric Apparatus, Method C*, the material was carried on a metal boat in a metal chamber, but even so the heat transfer characteristics were poor and the apparatus poor for rate determinations. In the first *Gas Volumetric Apparatus, Method E*, the material was supported in thin layers on metal fins, and in the *Large Volume Manometric Apparatus, Method F*, the bed of material was divided by vertical fins, so that both of these devices were excellent from the standpoint of heat transfer. In *Method F, the Second Gas Volumetric Method*, the material was placed in a glass U-tube and the heat conductivity was only fair.

*Method G, The Large Volume Manometric Apparatus*, was the most convenient method; the heat transfer characteristics were excellent; it permitted the determination of the rate at various temperatures but did not permit the variation of pressure.

It was noted in connection with the studies on 3-Ethoxy Co-Ox that reproducible rate curves at a given temperature and pressure were not obtained until the compound had been put through three or four cycles of oxygenation and deoxygenation. Data showing this is plotted in Figure 1.

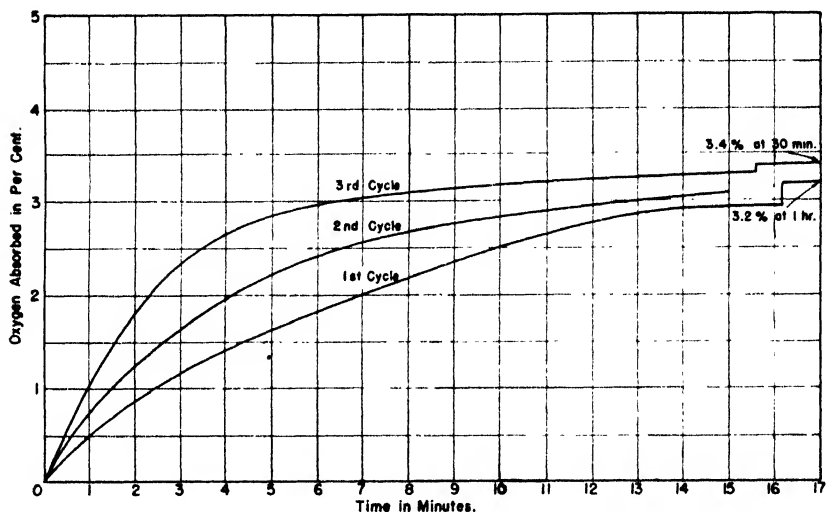


FIG. 1. Variation in the rate of oxygenation of 3-Ethoxy Co-Ox at 0° and 710 mm. Hg during the first few cycles.

#### METHOD A. DIRECT GRAVIMETRIC METHOD CAPACITY ONLY

Most of the measurements of oxygen-carrying capacity described in these papers were made by exposure of the material being tested to an atmosphere of oxygen at increased pressures, generally up to about 300 psig. These tests were carried out in a horizontal steel tube with a screw cap, the material being carried on a suitable boat. This type of apparatus permitted the capacity to be measured at only one temperature, not only because it would be difficult to jacket the bomb for heating or cooling media but also because of the difficulty of removing the boat bearing the material for weighing, at which time oxygen might be gained or lost to the atmosphere. This technique has been satisfactory for work with the parent, oxygen-carrying compound inasmuch as its working range is somewhat above room temperature and it does not lose its oxygen readily on exposure to air. However, it is known that there exists an optimum temperature of oxygenation above and below which oxygen is absorbed

to a lesser degree, and it became desirable to have available a method of testing compounds at various temperatures.

#### METHOD B. GAS EVOLUTION-NITROMETER APPARATUS

##### CAPACITY ONLY

Owing to the highly hygroscopic character of some of the oxygen-carrying compounds investigated, the direct gravimetric method of determining capacity was occasionally inapplicable, owing to the impossibility of weighing the compound in contact with air. In order to circumvent difficulties of this kind a method was devised in which the oxygen was expelled from the oxygenated material and collected and measured.

This apparatus consisted of a source of carbon dioxide, a drying train, a glass tube in which the boat of material was placed, and a nitrometer. Dry ice was used as a source of carbon dioxide and the dry ice container was connected with a pressure regulator to control the rate of flow through the apparatus to the nitrometer. The carbon dioxide gas evolved from the dry ice was passed through a U-tube containing phosphorous pentoxide on asbestos. This was found necessary since the dry ice always contained moisture condensed on its surface which was carried off with the carbon dioxide gas and formed ice in the tube containing the boat at low temperatures.

The procedure employed in determining the capacity of a sample using this apparatus was the following: A sample of the compound was deoxygenated under a vacuum at 100<sup>°</sup> and then the boat placed in a vacuum desiccator which was immediately evacuated before the boat had cooled appreciably. After cooling to room temperature the vacuum was quickly released and the boat of deoxygenated compound weighed immediately. This weighing was made by first placing the approximate weights on the balance as determined by previous weighing, so that only about fifteen seconds were required to obtain the final weight. This sample was oxygenated in a bomb under 200 pounds oxygen pressure for fifteen minutes, and then weighed immediately after removing from the bomb. The boat was then placed in the deoxygenation tube of the capacity apparatus and the tube closed. The tube containing the boat was surrounded by dry ice and then carbon dioxide passed over the boat containing the compound until all the air had been swept out, as shown by micro-bubbles in the nitrometer. The nitrometer was filled with 36 per cent potassium hydroxide containing a trace of barium chloride added to prevent the formation of foam in the top of the nitrometer. The oxygen in the sample was released and collected in the nitrometer by first removing the dry ice packing and then gradually heating the tube containing the boat with the sample with an infra-red lamp. The tube was swept out with carbon dioxide until micro-bubbles were obtained. The capacity of the sample was calculated from the volume of oxygen collected as

will be subsequently shown. After cooling to room temperature in an atmosphere of carbon dioxide, the boat containing the deoxygenated sample was again weighed in order to serve as a comparison for the volumetric method.

It was found that the completely oxygenated 3-methoxy compound lost oxygen slowly at room temperature under atmospheric pressure. Under a diminished oxygen pressure, produced either by a vacuum or a stream of carbon dioxide, it evolved a large portion of its absorbed oxygen. It was also found that the parent compound upon being placed in the apparatus lost weight slowly in an atmosphere of carbon dioxide. Because of these observations it was found necessary to cool the tube containing the weighed sample of oxygenated material with dry ice so that the compounds would retain their absorbed oxygen until the air present in the tube at the time of the introduction of the sample was completely swept out.

Since the oxygen collected was measured over a potassium hydroxide solution, correction was made for the vapor pressure of the solution as follows: from the *International Critical Tables*, Volume III, page 528, the formula given for calculating the vapor pressure of aqueous solutions was

$$100 R = \frac{100 (P_0 - P)}{M P_0} \text{ where}$$

$P_0 = \text{V.P. H}_2\text{O}$ ;  $M = \text{moles/1,000 g. H}_2\text{O}$ ;  $P = \text{V.P. of solution}$ .  
For potassium hydroxide, at  $25^\circ$ , when  $M = 10$ ,  $100 R = 5.62$ .

$$\text{Hence } P = P_0 - \frac{100 R \cdot P_0 M}{100} = 24 - \frac{5.62 \cdot 24 \cdot 10}{100} = 10.5 \text{ mm.}$$

This vapor pressure correction is valid only when the gas is measured over pure 10  $M$  potassium hydroxide. This obviously was not done since some potassium carbonate would be formed by absorption of the carbon dioxide used to sweep out the apparatus. However, since the vapor pressure values in *I.C.T.* for potassium carbonate solutions closely parallel those for potassium hydroxide, it was assumed that the error would be negligible if fresh 10  $M$  potassium hydroxide was used for each run.

The above method of measurement was checked by transferring several gas samples measured over potassium hydroxide to a water burette and again measuring the volume. Volumes of 30.0 and 50.0 ml. became 30.5 ml. and 50.8 ml., respectively, over water; the calculated volumes were 30.52 and 50.87 ml. It was thereby concluded that at  $25^\circ$  a vapor pressure correction of 10.5 mm. is correct, and this value was used for calculating results tabulated below.

As a check, the capacity of several preparations was determined by the gas evolution-volumetric method and the direct gravimetric method.

	Capacity, as percentage	
	Gas Evolution Method	Direct Gravimetric Method
Co-Ox		
(Preparation 1) . . . . .	4.58	4.60
Co-Ox		
(Preparation 2) . . . . .	4.81	4.68
3-Methoxy Co-Ox		
(Preparation 1) . . . . .	3.98	4.06
3-Methoxy Co-Ox		
(Preparation 2) . . . . .	4.17	4.21
3-Methoxy Co-Ox		
(Preparation 3) . . . . .	4.21	4.37

In the case of 3-Methoxy Co-Ox the high results by the gravimetric method are probably due to the absorption of moisture during the weighing process.

#### METHOD C. DIFFERENTIAL MANOMETRIC APPARATUS

##### CAPACITY AND RATE IN OXYGEN

This apparatus, shown in Figure 2, consisted of a row of four horizontal chambers suitably interconnected. The central chambers *B* and *C* were made equal in volume (about 700 ml.), the outer chambers, *A* and *D*, being of equal volume (about 75 ml.). Chamber *A* was fitted with a screw cap which could be removed so that a sample of material to be tested could be placed in the chamber on a suitable boat. Chambers *A* and *D* were interconnected through valves 5 and 6, and could be evacuated through the pipe between 5 and 6. Chambers *B* and *C* were interconnected through valves 1 and 2, and were charged with oxygen under pressure, the oxygen pressure being measured by a gauge on the oxygen line 6. Chambers *B* and *C* could be brought to the same pressure and then closed off from each other. The large chambers were also connected to the adjacent outer chambers through valves which could be opened to permit the oxygen to expand from the large chamber into the adjacent, small chamber. That is, the oxygen in *B* could be expanded through valve 3 into *A*, and the oxygen in *C* expanded through valve 4 into *D*. A differential manometer was connected between *B* and *C*. As the material contained in *A* absorbed oxygen, the pressure of the gas in *A* plus *B* fell below that in *C* plus *D*, and the pressure difference was recorded on the manometer. As will be seen from the mathematical development given below, the actual pressure within the apparatus was not involved in the determination of the capacity of a material being tested.

The chambers of this apparatus were constructed of hexagonal, brass bushing of suitable size. The chambers were connected by means of 0.25 inch copper tubing. The valves were especially constructed of brass with stainless steel needles. The glass manometer was sealed to the copper tubing by a fused copper-glass seal. The screw cap of a chamber had a hexagonal head and was threaded about twenty threads to the inch. The



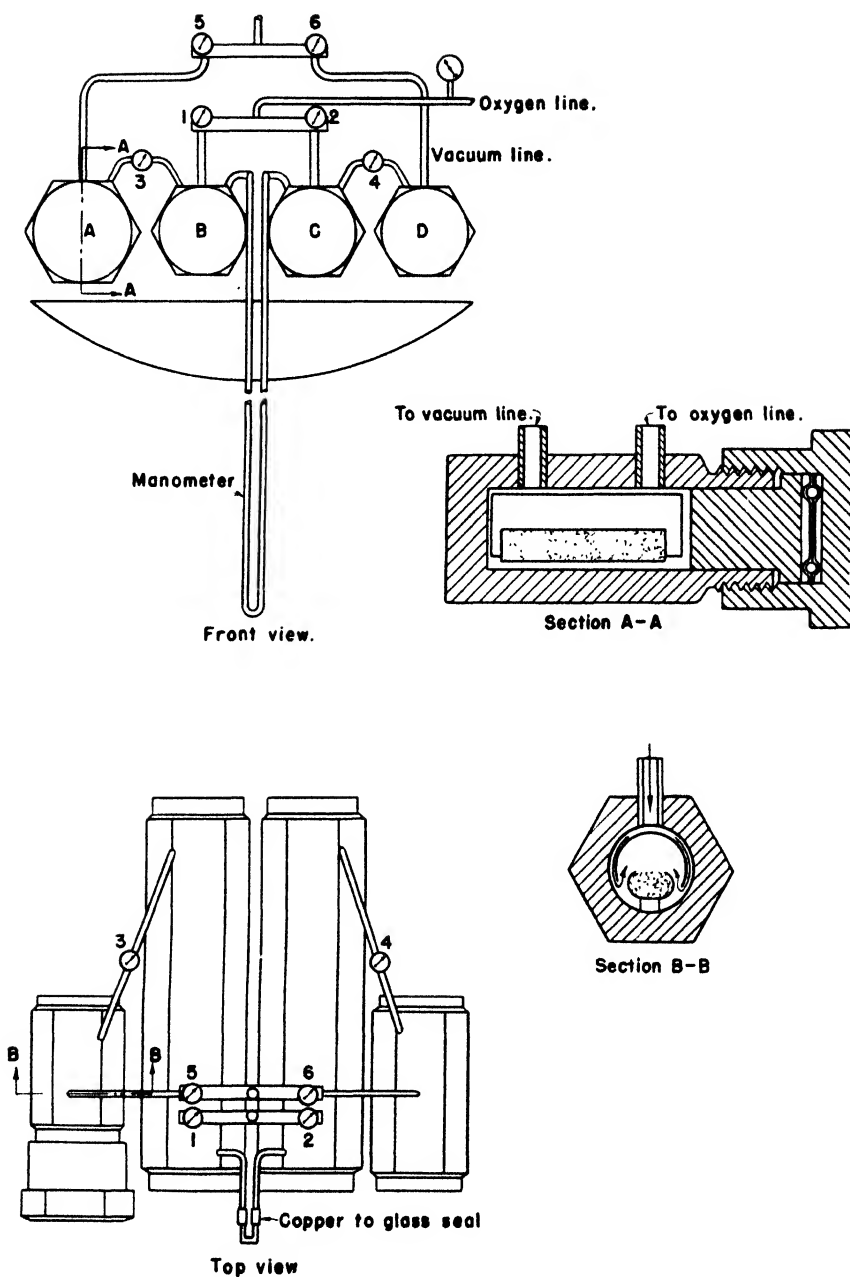


FIG. 2. Differential manometric apparatus for the determination of oxygen-carrying capacity.

collar which actually closed Chamber *A* was backed up by a thrust ball bearing such that the collar did not turn when the screw cap was tightened. A well insulated box serving as a constant temperature bath was mounted on a hydraulic jack so that it could be raised up about the apparatus. The box was equipped with a 0.25 h.p. refrigeration unit and had the copper tubing cooling unit around the inside walls. An alcohol-water mixture was placed in the box so that the apparatus could be operated at a temperature as low as  $-20^{\circ}$ .

The sequence of manipulations in the operation of this instrument was as follows: A weighed sample of deoxygenated material contained on a boat was placed in Chamber *A* and the sealing collar, gasket, and screw cap put in place and tightened. Valves 3 and 4 were closed. Valves 5 and 6 were opened, chambers *A* and *D* were evacuated and then valves 5 and 6 were closed. The entire apparatus was immersed in a bath and sufficient time allowed for the apparatus to assume the temperature of the bath. Valves 1 and 2 were opened, chambers *D* and *C* charged with oxygen to a pressure somewhat higher than the final pressure at which the capacity was to be determined, and valves 1 and 2 were then closed. Valves 3 and 4 were then opened simultaneously and carefully to avoid any pressure differential which might force the mercury of the differential manometer into chambers *B* or *C*. Sufficient time was allowed for the compound to be completely saturated with oxygen and the difference in the level of the mercury in the manometer was read. From this pressure difference, the weight of the sample, and the pressure difference of a blank determination, the capacity of the material was calculated using the following formula:

$$\text{Percentage Oxygen Absorbed} = \frac{(100) \ 32 \ (\delta P_s - \delta P_b) \ (V_{A+B} - \frac{W_s}{d})}{W_s \ R \ T}$$

where

- $W_s$  = weight of sample
- $\delta P_s$  = pressure difference observed
- $\delta P_b$  = pressure difference observed during blank run
- $V_{A+B}$  = combined volume of chambers *A* and *B*
- $d$  = density of sample (taken as 1.5 for these compounds)
- $R$  = the Gas Constant
- $T$  = the absolute Temperature

This formula was developed as follows, using the further definitions:

- $V_A, V_B, V_C, V_D$  = volumes of chambers *A*, *B*, *C*, and *D*, respectively
- $V_{C+D}$  = combined volume of chambers *C* and *D*
- $P_{A+B}$  = pressure in chambers *A* and *B* when interconnected (valve 3 open)
- $P_{C+D}$  = pressure in chambers *C* and *D* when interconnected (valve 4 open)
- $n_A, n_B, n_C, n_D$  = number of moles of oxygen in *A*, *B*, *C*, and *D*, respectively

- $n_A + n_B$  = number of moles of oxygen in *A* plus *B* when inter-connected  
 $n_C + n_D$  = number of moles of oxygen in *C* plus *D* when inter-connected

At the beginning, valves 3 and 4 are closed, 1 and 2 open and *B* and *C* charged with oxygen, and, valves 5 and 6 open and *A* and *D* evacuated. Valves 1, 2, 5, and 6 are then closed and the following conditions prevail:

$$\begin{aligned}
 P_A &= P_D & (= 1 \text{ mm. or less}) \\
 P_B &= P_C & (5 \text{ to } 250 \text{ pounds pressure}) \\
 P_A V_A &= n_A RT & \text{and a similar equation for } B, C, \text{ and } D
 \end{aligned}$$

In a blank determination, no compound is placed in *A* and the expansion is carried out. If the construction were perfect  $V_A + V_B$  would equal  $V_C + V_D$ , and  $P_{A+B} = P_{C+D}$ . Since this is not actually the case, a slight pressure difference  $\delta P_b$  is obtained. Applying the gas laws:

$$\begin{aligned}
 (1) \quad P_{A+B} (V_A + V_B) &= (n_A + n_B) RT \\
 (2) \quad P_{C+D} (V_C + V_D) &= (n_C + n_D) RT
 \end{aligned}$$

Subtracting (2) from (1)

$$(3) \quad \delta P_b = P_{A+B} - P_{C+D} = \frac{(n_A + n_B) RT}{V_A + V_B} - \frac{(n_C + n_D) RT}{V_C + V_D}$$

When an oxygen absorbing material is present, let

$n_s$  = moles of oxygen absorbed by compound

$\delta P_s$  = observed pressure difference

then

$$\begin{aligned}
 (4) \quad P_{A+B} (V_A + V_B) &= (n_A + n_B - n_s) RT \\
 (5) \quad P_{C+D} (V_C + V_D) &= (n_C + n_D) RT
 \end{aligned}$$

and

$$(6) \quad \delta P_s = P_{A+B} - P_{C+D} = \frac{(n_A + n_B - n_s) RT}{V_A + V_B} - \frac{(n_C + n_D) RT}{V_C + V_D}$$

$$(7) \quad \delta P_s = \frac{(n_A + n_B) RT}{V_A + V_B} - \frac{(n_C + n_D) RT}{V_C + V_D} - \frac{n_s RT}{V_A + V_B}$$

introducing equation (3)

$$(8) \quad \delta P_s = \delta P_b + \frac{n_s RT}{V_A + V_B}$$

Owing to the variation of the diameter of the copper tubing, the volume of Chamber *B* is not exactly equal to the volume of Chamber *C* and the volume of *A* not equal exactly to the volume of Chamber *D*. Fortunately, this difference can be corrected without much difficulty as indicated in the above mathematical development.

As will be seen from the above mathematical analysis, it was necessary that the combined volume of chambers *A* and *B* must be known. This

volume was determined by two different methods. In one method the volume of chambers *A* plus *B* was determined by expanding air from chambers *A* plus *B* into a flask of known volume, and measuring the change in the pressure of the system by means of the manometer. The flask was attached to the evacuation tube (between valves 5 and 6), valves 1, 4, and 6 were closed, and valves 2, 3, and 5 were opened. Thus, chambers *A* and *B* were connected to each other, to the flask of known volume, and to the manometer. The second arm of the manometer remained open to the atmosphere by way of Chamber *C*, Valve 2, and the oxygen line. The volume of the connecting tube between Valve 5 and the flask was determined independently by a similar method and its volume subtracted in the determination of the volume of *A* plus *B* as just described. The volume of the flask itself was determined by weighing it full of water. The volume of chambers *A* plus *B* was found to be 779, 781, and 781 ml. by three determinations. These values may be slightly in error because of the change in the volume of chambers *A* plus *B* as the position of the mercury in the manometer changed; this error has been determined to be less than 2 ml., and thus so small that it may be neglected.

The volume of chambers *A* plus *B* was determined also by calibration of the apparatus against a sample of the parent, oxygen-carrying compound whose capacity had been very carefully determined by measuring the increase in weight on standing in pure, dry oxygen at atmospheric pressure (in this case saturation should not be made with high pressure oxygen because it was found that after complete saturation, the compound is still capable of absorbing a few tenths per cent of oxygen more, possibly by adsorption). The results by this method checked the results of the first method within 2 ml.

This apparatus made possible the determination of the oxygen-carrying capacity of the compounds studied at a variety of temperatures and pressures. With some compounds these determinations cannot be made in the usual manner, inasmuch as the compounds frequently lose their oxygen spontaneously on being removed from an atmosphere of oxygen and cannot therefore be weighed sufficiently rapidly to prevent error. Also, some compounds are hygroscopic in nature and cannot be exposed for weighing.

This apparatus was also used for the determination of the rate of oxygenation in oxygen of certain compounds.

#### METHOD D. GRAVIMETRIC RATE METHOD

##### CAPACITY AND RATE IN AIR OR OXYGEN

In this procedure the material was placed in a U-tube, glass wool plugs inserted to prevent loss of compound, and the material oxygenated by the passage of a rapid stream of air through the tube. After a measured time the flow of air was stopped, and the U-tube closed, brought to room temperature and weighed. The material was then deoxygenated and the

process repeated using a different time interval. The deoxygenation was effected by placing the U-tube in a beaker of hot water and passing a slow stream of nitrogen through it. Rates of oxygenation at various temperatures were obtained by placing the U-tube in a liquid bath at the desired temperature and allowing sufficient time for temperature equilibrium to be established.

By this method the rates of oxygenation of 3-Methoxy Co-Ox at various temperatures were determined (*see* Paper VI, Figure 1).

#### METHOD E. GAS VOLUMETRIC APPARATUS CAPACITY AND RATE IN OXYGEN

This apparatus devised for measuring the rate of oxygenation. Figure 3, consisted of a gas holder, a reaction chamber, and a water manometer. Water was used as the retaining liquid in the gas holder, therefore the oxygen was delivered saturated with moisture. The gas holder was equipped with a modification of the Mariotte bottle so that it delivered the oxygen at a constant pressure, either greater or less than atmospheric pressure. The gas holder held about 2.5 liters and was calibrated with water delivered from a Morse-Blalock bulb.

The reaction vessel was jacketed and the compound was carried on a metal tube with circular fins spaced about 7 mm. apart along the tube. This tube slipped snugly into the reaction vessel, and provided ample heat contact between the compound and the circulating liquid. Water from a large, well insulated carboy was passed successively through the jacket and the central metal tube bearing the fins; the thermometers were placed in the inflow and outflow water and the flow of water was adjusted so that these temperatures were the same throughout a run, thus insuring that the compound remained at a constant temperature. At the conclusion of a run, steam was passed through the jacket for forty minutes to deoxygenate the compound.

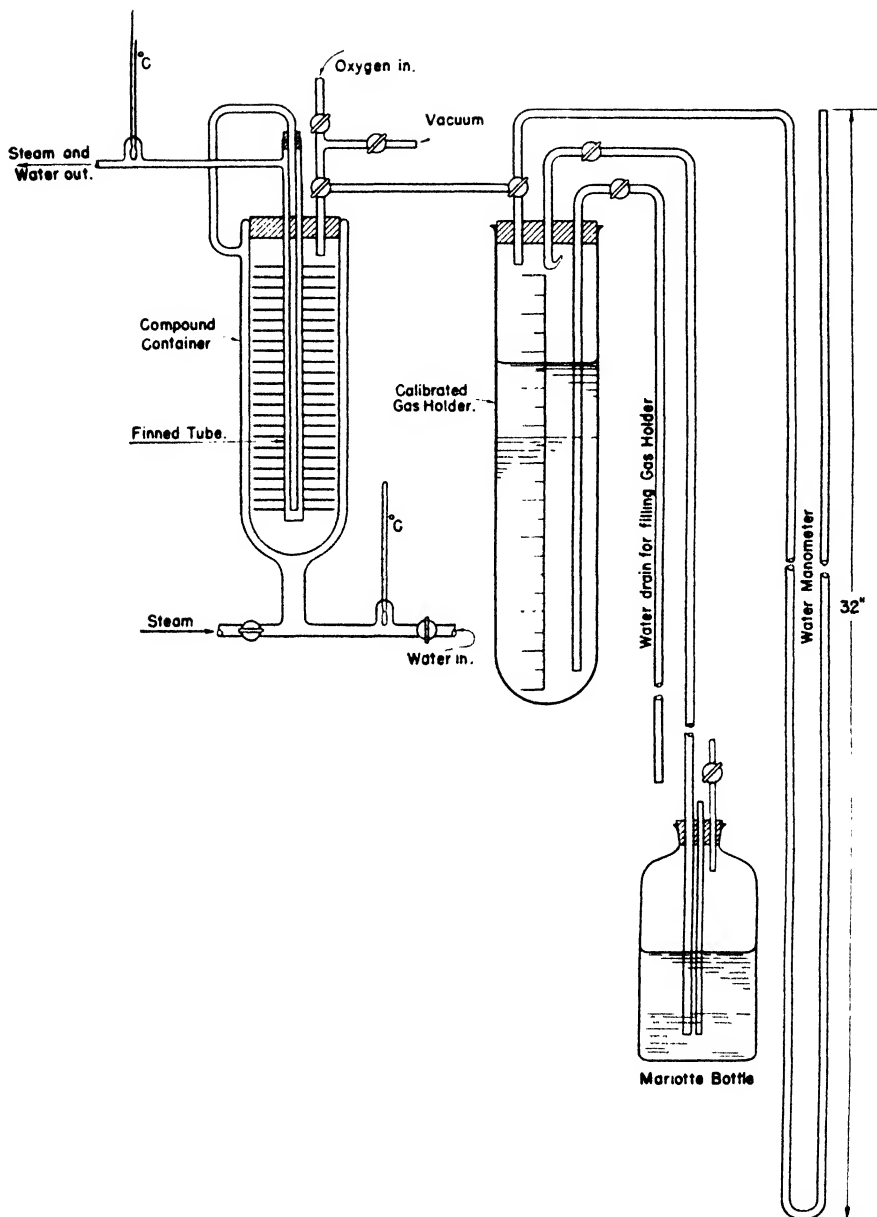
A water manometer was used to measure the pressure at which the gas was delivered. Time was measured with a stop watch and in general readings of time and gas volume were made every thirty seconds.

The purity of the oxygen used was determined by the usual gas analysis methods using the alkaline hydrosulfite reagent. It was found that commercial tank oxygen was about as good as any made by heating a mixture of potassium chlorate and manganese dioxide following evacuation to remove residual air from the generator. Aqueous retaining liquids were freed of air by boiling or by sweeping for some time with oxygen and were subsequently protected from air.

With this apparatus rates of oxygenation were determined on Co-Ox at pressures varying from 200 to 870 mm. of mercury, and at temperatures from  $-7^{\circ}$  (using a refrigerated brine) to  $41^{\circ}$  (*see* Paper III).

#### METHOD F. SECOND GAS VOLUMETRIC METHOD

The apparatus is shown in Figure 4. The U-tube was filled with a weighed sample of the compound. The sample was then deoxygenated



**FIG. 3.** First gas volumetric apparatus used for measuring rate of oxygenation.

and activated by immersing the U-tube in a bath maintained at  $120^{\circ}$ . At the same time a stream of dry nitrogen was passed slowly through the U-tube to sweep out the oxygen and water. As soon as the deoxygenation and activation was complete, in approximately fifteen minutes, the stopcocks on the U-tube were closed and the U-tube installed in the apparatus. Ample time was allowed for the compound to come to the temperature of the bath. Then the U-tube and train up to the oxygen tank was evacuated. The buret was filled with oxygen from the cylinder. A salt solution was used as retaining liquid in the buret so as to give the oxygen

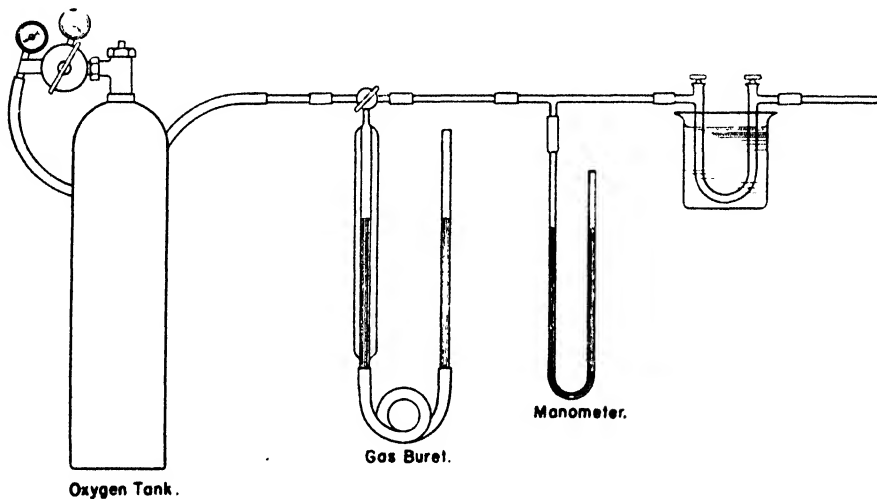


FIG. 4. Second gas volumetric apparatus used for measuring rate of oxygenation.

contained in it the desired moisture content. When the evacuation was complete, the vacuum pump was stopped and the stopcock on the U-tube closed. Then the stockcock on the buret was turned in such a manner as to admit the oxygen to the U-tube. The leveling bulb was so handled that the pressure of the oxygen remained as desired through the run. Buret readings were taken at timed intervals, and from the volume of oxygen absorbed and the weight of the sample, the weight per cent of oxygen absorbed was calculated. The method was used principally in the determination of the rate of oxygenation of 3-Nitro Co-Ox (Paper V).

#### METHOD G. LARGE VOLUME MANOMETRIC APPARATUS CAPACITY AND RATE IN OXYGEN

The change in pressure of the system as oxygen is absorbed furnishes a convenient way of following the absorption. It is free of manipulation during the absorption and gives an uninterrupted record of an individual absorption experiment. Unfortunately it is limited to determining the rate of oxygenation in pure oxygen only and cannot be used with air, owing to the accumulation of the residual nitrogen about the compound. Although

the pressure is not strictly constant during the run, the variation is rather small and has an insignificant effect on the rate of oxygenation of the material studied.

The apparatus, shown in Figure 5, consisted of a 5-liter round bottom flask fitted with a two-hole rubber stopper firmly wired in place. This flask was placed in a constant temperature water bath the temperature of which was kept constant to within  $0.1^{\circ}$ . This flask was connected to an open arm mercury manometer and to the sample tube, vacuum pump, and oxygen cylinder through a suitable arrangement of 3-way stopcocks. The

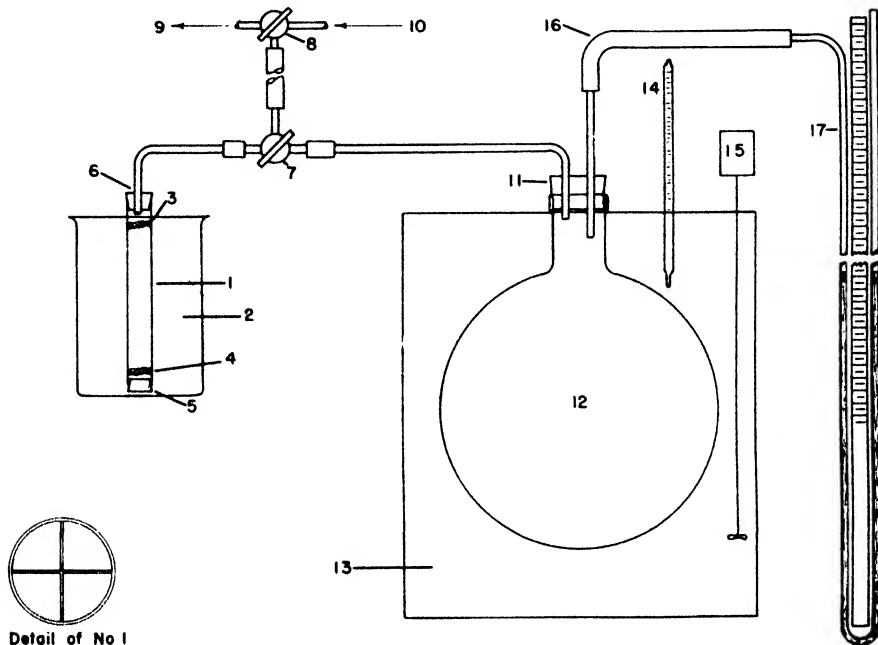


FIG. 5. Large volume manometric method for measuring rate of oxygenation.

sample tube was constructed of an 8 inch length of 1 inch standard copper pipe and had 4 copper fins soldered inside in the form of a +. Each end of the copper pipe was wadded with cotton and stoppered tightly with a rubber stopper.

The apparatus was operated in the following manner: A 20 g. sample of compound was deoxygenated and activated in a boat at the required temperature. It was weighed in the boat, then heated again, and finally transferred quickly to the copper sample tube while hot. With reasonable care, the weight of the sample could be obtained accurately to 0.01 g. which is much less than the experimental error of the apparatus in general. The sample tube was assembled in the apparatus and a 2-liter beaker of boiling water placed around it. The system was evacuated and the sample heated for about fifteen minutes to deoxygenate the material.



A water bath at the desired oxygenation temperature was placed around the sample tube and twenty minutes allowed for cooling. After this, stopcock 8 was closed, the vacuum pump stopped, and then stopcocks 7 and 8 turned so as to open the oxygen line to the Flask 12, keeping the sample tube evacuated. The flask was filled with pure dry oxygen at approximately atmospheric pressure. Stopcock 8 was then closed and sufficient time allowed for the oxygen to come to the temperature of the bath. The bath was always kept at room temperature and the stirrer operated to maintain a uniform temperature. The temperature of the sample and bath, and the pressure in the oxygen flask were recorded. Stopcock 7 was opened, admitting oxygen to the sample, and the progress of oxygenation followed on the manometer.

The blank manometer reading due to expansion of the oxygen into the evacuated sample tube was determined and applied. This was 1.2 cm. of mercury for a 16–20 g. sample. For smaller samples this became 1.3 cm. Check results were obtained in the determination of this blank and the blank was determined for each sample. This was done by evacuating the system, filling the flask with dry nitrogen and then allowing the gas to expand into the sample tube.

In early experiments with this apparatus a pyrex test tube was used to hold the sample. Duplicate runs were consistent but a very marked increase in the rate resulted when the copper tube with internal fins was substituted for the pyrex tube. This was, of course, due to the superior thermal conductivity of the copper sample tube.

In several runs the weight of sample taken was varied and shown not to affect the results.

The time required to cool the hot, freshly deoxygenated sample in the copper sample tube was varied from ten to forty minutes, to determine the time necessary to bring the sample to the temperature of the bath. It was found that twenty minutes was satisfactory.

The results with this apparatus were very consistent. The rates of oxygenation of 3-Ethoxy Co-Ox (Paper VII) and of the various mixed compounds (Paper XI), were determined with this apparatus.

# STUDIES ON OXYGEN-CARRYING COBALT COMPOUNDS

## XIV. THE DESIGN OF APPARATUS FOR THE MANUFACTURE OF OXYGEN USING Co-Ox AND ITS DERIVATIVES

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The reversible absorption and release of oxygen by disalicylalethyl-enediimine cobalt (Co-Ox) and certain of its derivatives makes possible the separation of oxygen from the atmosphere. In brief, the process involves exposure of the oxygen-carrier to air so that it absorbs oxygen, of removing the residual nitrogen, of then causing the material to release its oxygen so that it may be collected in pure form. and of continually repeating this sequence. There are a number of ways in which this cycle of oxygenation and deoxygenation may be carried out:

1. Temperature variation processes
  - a. Batch (intermittent delivery from a single bed, steady delivery from a multiple bed)
    - (1) Stationary bed
    - (2) Agitated bed
  - b. Circulating solid
  - c. Circulating oil suspension
2. Adiabatic processes
  - a. Single bed
  - b. Interlacing double bed

Batchwise operation with a stationary bed appeared at first to be the simplest of these with respect to the construction, but actually posed certain difficult problems—principally that of heat transfer. The parent oxygen-carrying compound, Co-Ox, must be cooled to about 15° and subjected to air pressure of about 100 pounds pressure to effect the oxygenation rapidly. It must be heated to about 65° to expel the oxygen at atmospheric pressure. 3-Methoxy Co-Ox (Paper VI) operates at lower temperatures for both oxygenation and deoxygenation. The thermal conductivity of both materials is very low and the heat of reaction is quite high, of the order of 20,000 calories per gram mole of oxygen, heat being liberated on the absorption of oxygen. As a consequence, in a stationary bed apparatus the material must be placed in close proximity to cooling and heating surfaces. Agitation, on the other hand, increases the rate of heat transfer but introduces difficulties in filtering the fine, dusty oxygen-carrier from the gas streams, makes it necessary to evacuate a greater amount of residual air, and makes necessary certain precautions

to prevent dust explosions. In either the stationary bed or the moving bed apparatus a considerable quantity of metal must be alternately cooled and heated along with the compound.

In the circulating solid type of apparatus, the material is made to circulate about in an apparatus in which the cooling and oxygenation are effected in one chamber and the heating and deoxygenation in a second, a suitable transferring device being employed to effect the transfer from one chamber to the other and back. Such an apparatus delivers a steady flow of oxygen.

In the adiabatic method of operation, the difficulties of transferring heat into and from the material are obviated and the oxygenation and deoxygenation effected by changing the pressure of the system. Preliminary work using the parent compound yielded unsatisfactory results for this type of operation, the pressure required being too great. It is possible that a successful adiabatic apparatus could be devised using 3-Ethoxy Co-Ox, the rate of oxygenation of which is practically independent of temperature.

#### STATIONARY BED PROCESS

In our first designs of apparatus for the manufacture of oxygen it was found that attempts to heat and cool a deep bed of material were impracticable, owing to the poor thermal conductivity characteristics of the material. The recirculation of cold air over the material to cool and oxygenate the material, and of hot oxygen to heat and deoxygenate it, was considered. It was found that nearly 50 cubic feet of oxygen at 100° was required to heat one pound of compound to the deoxygenation temperature and to deoxygenate it. Thus, a huge volume of gas had to be circulated to secure the desired temperature change. This method had the advantage that the material could be insulated from the walls of the container and the heat capacity of the latter eliminated. But the excessive amount of pumping required made the method impracticable.

In another apparatus an attempt was made to reduce the amount of the circulating gases required to cool and heat the compound. Copper coils were embedded in the compound every two inches through the container. Copper gauze was soldered onto the coils to secure greater surface. Steam or cold water was circulated through the compound. It was thought that the stream of the gas would carry the heat from the coils to the compound (or vice versa), after which the gas would again come in contact with and assume the temperature of another coil. The rates of cooling and heating were again too low, probably because of a film of compound clinging to copper and gauze. A possible way to eliminate this trouble would be to put the coil in a cage so that no compound could touch it while the recirculating gas was able to come in intimate contact with the coil; this would have introduced a great many filters and was not tried.

In a third apparatus the cooling was accomplished entirely by circulating cold water, and the heating by circulating steam—only sufficient

air being passed over the compound to ensure complete oxygenation. The compound was packed between copper plates spaced about half an inch apart. Soldered to the plates were copper tubes through which either steam or cooling water could be passed. It was found that if the compound were packed in the mesh of an automobile radiator, and cooling water or steam passed through the radiator, excellent heat transmission to and from the bed compound was obtained.

On long-time operation of such a bed, the compound set up to a solid which could be removed from the metal container only with the greatest difficulty.

#### AGITATED BED PROCESS

Two apparatus falling under this classification were built. In the first a range boiler, 12 inches in diameter and 36 inches long, was used for the reaction vessel. This was surrounded by a jacket through which steam or cold water could be passed. A stirrer, somewhat resembling the rotating, cutting blades of a lawnmower, was mounted with its shaft in the axis of the tank, the axis being horizontal. Strips of rubber were placed along the edges of the blades to wipe the walls of the tank. Air was introduced through a pipe passing through the jacket and welded to the tank. The discharge gases were withdrawn through a centrifugal dust separator. This apparatus worked fairly well but was rather slow, owing to the rigid adherence of the compound to the walls of the tank and the consequent decrease in heat transmission.

In the second apparatus the tank containing the compound was made to revolve. The tank was 12 inches in diameter and 36 inches long. The interior of this tank was given a high polish by buffing with emery. Nine brightly polished copper fins, 2 inches wide and each running the entire length of the tank, were soldered to the walls of the tank. This about doubled the area of the metal surface, making a total of about 18 square feet. The cement-mixer action of this design, coupled with the bright polishing of the metal surfaces and the large area of the latter, greatly improved the heat transfer over the apparatus described just previously. The apparatus was charged with 20 pounds of Co-Ox. Using steam, the deoxygenation was accomplished in about ten minutes. The cooling and oxygenation took fifteen to twenty minutes, the longer time being required since the difference between the temperature of the cooling water and 20°, the optimum temperature for oxygenation, was considerably less than the difference between 65°, the deoxygenation temperature, and 100°, the temperature of the steam. Since about ten minutes more was required to evacuate the tank to remove the residual air after oxygenation and to pump off the oxygen remaining in the tank, the time required for a cycle was thirty-five to forty minutes. The purity of the oxygen produced by this apparatus depended on the completeness with which the residual air was removed prior to the deoxygenation step, though 96 per cent pure oxygen was typical. The details of construction are shown in Figure 1. The sequence of operations is obvious.

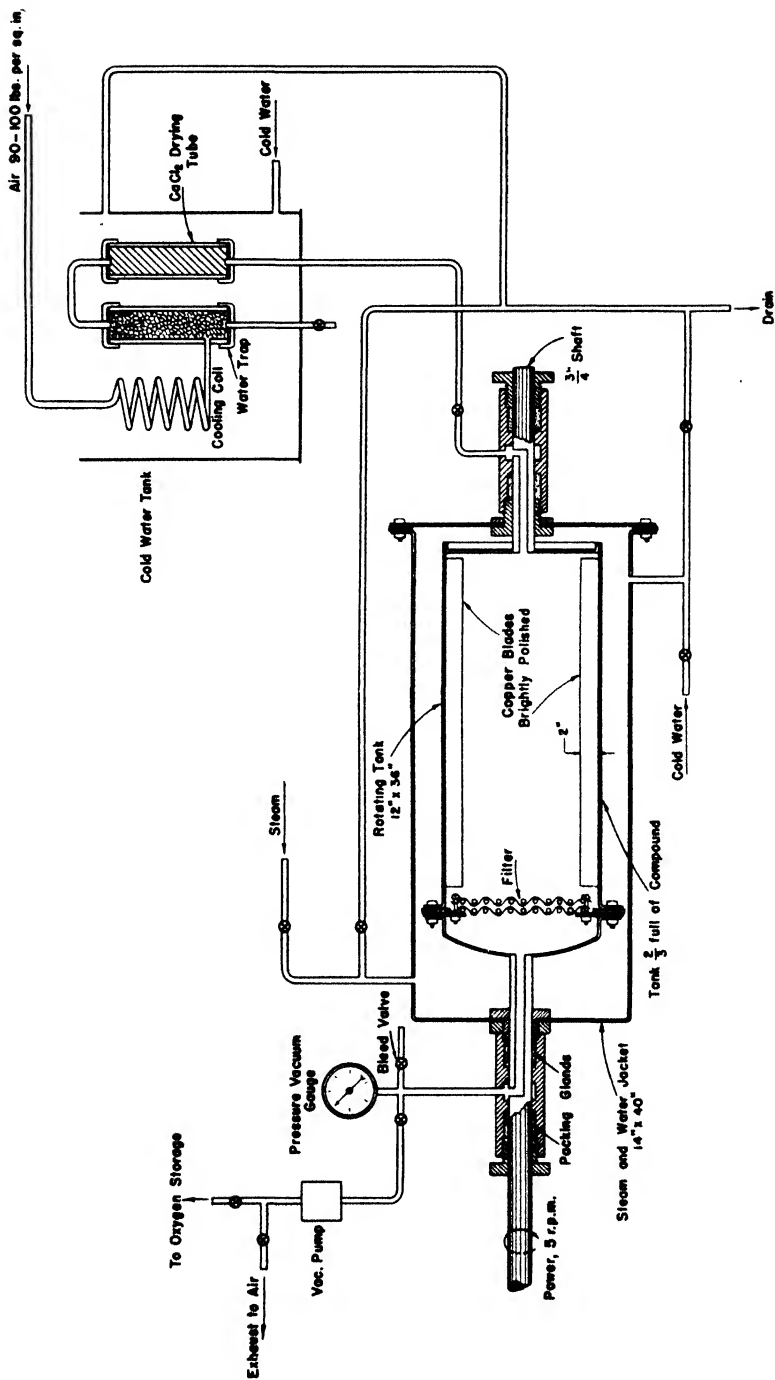


Fig. 1. Agitated bed apparatus used for the manufacture of oxygen using Co-Ox.

## CONTINUOUS CIRCULATING SOLID APPARATUS

The circulating solid type of apparatus has certain inherent advantages which make it of particular interest. The essential feature of the circulating solid apparatus is that the oxygenation and the deoxygenation of the oxygen-carrying material are carried out in separate chambers. The solid, oxygen-carrying material is first conveyed through the oxygenation chamber where it is cooled and exposed to air, is then transferred to the deoxygenation chamber where it is heated and where it releases its oxygen, and is then transferred back to the oxygenation chamber. This is shown schematically in Figure 2.

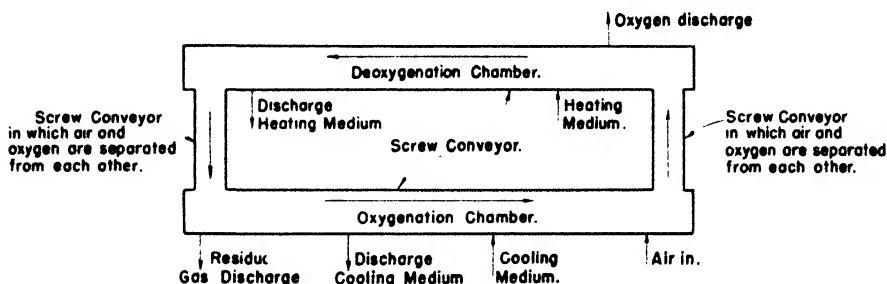


FIG. 2 . Schematic diagram of circulating solid apparatus.

Using the parent oxygen-carrying compound, Co-Ox, a pressure of about 100 pounds per square inch is required to effect the oxygenation rapidly. 3-Methoxy Co-Ox, however, oxygenates rapidly at atmospheric pressure. One of the principal problems in the design of a circulating solid apparatus is the transfer of the material from the oxygenation chamber to the deoxygenation chamber. Obviously this is easier if the oxygenation and deoxygenation chambers are operated at the same pressure rather than different pressures. For this reason the 3-Methoxy Co-Ox was used in the circulating solid apparatus to be described, in which case the pressure was atmospheric throughout the machine.

The rate of oxygenation of 3-Methoxy Co-Ox at various temperatures is given in Paper VI, Figure 1. As will be observed, an optimum exists at about 0° in the rate of oxygenation, and at temperatures in the neighborhood of 0° or slightly above, the oxygenation is about 90 per cent complete in eight minutes. The theoretical oxygen-carrying capacity of 3-Methoxy Co-Ox is 4.15 per cent oxygen. Using a cycle in which the time of oxygenation is about eight minutes, the oxygenation can then be effected using air at atmospheric pressure. The temperature of deoxygenation of 3-Methoxy Co-Ox against oxygen at atmospheric pressure is about 80°. The deoxygenation takes place practically instantaneously. A time of fifteen minutes appeared possible for the circulation of the material completely through the apparatus, the material being cooled to 5° in the oxygenation chamber and heated to 80° in the deoxygenation chamber. Assuming the effective amount of oxygen carried to be 3.5

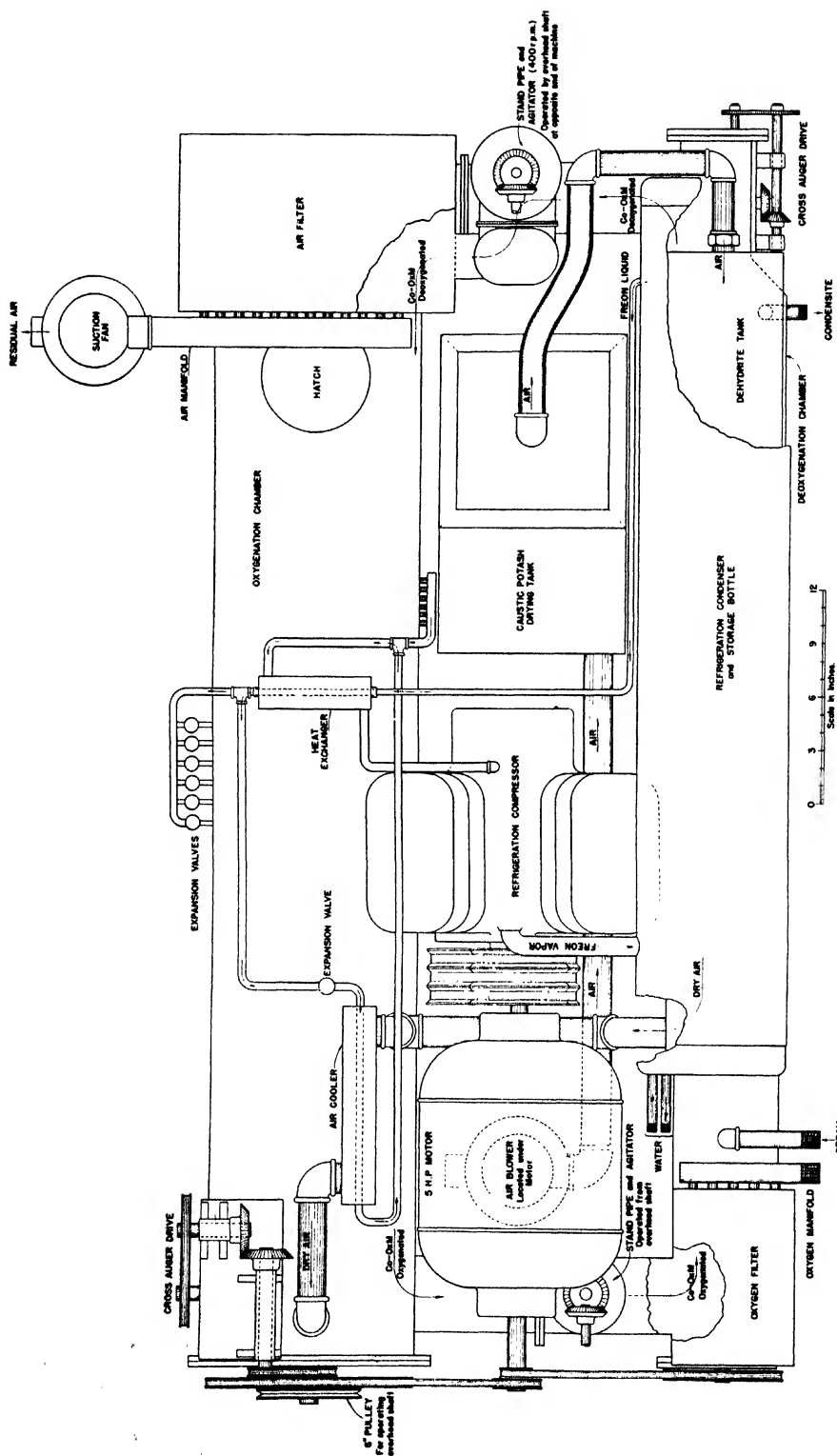


FIG. 3. Plan of circulating solid apparatus for the manufacture of oxygen using 3-Methoxy Co-Ox

per cent and the material to make four cycles per hour, about 1.6 cubic feet of oxygen are carried per pound of 3-Methoxy Co-Ox. A unit to produce 100 cubic feet per hour would require 62.5 pounds of the material.

The properties of 3-Methoxy Co-Ox made it possible to operate this apparatus at essentially atmospheric pressure, the deoxygenation being carried out at a pressure only very slightly higher than that at which the oxygenation was effected. The device used to transfer the solid material from one chamber to the other thus had to work against a pressure of a



FIG. 4. Circulating solid apparatus for the manufacture of oxygen using 3-Methoxy Co-Ox.

few inches of water. The transferring devices consisted of a compacted bed of 3-Methoxy Co-Ox which was slowly moved by augers and which was so constructed that a slight flow of oxygen was maintained through the bed and out of the deoxygenation chamber to the oxygenation chamber—so as to continually sweep the air from the compound and maintain the purity of the oxygen produced. The oxygenation chamber was cooled by mechanical refrigeration to lower the temperature of the 3-Methoxy Co-Ox and to remove the heat of oxygenation. The deoxygenation chamber was heated to raise the temperature of the oxygenated material to the point where its oxygen was expelled, and to supply the heat of deoxygenation. The air used was well dried and suitable provision was made for removing the finely powered 3-Methoxy Co-Ox from the air and oxygen streams. An attempt was made to make the apparatus as compact as feasible.

The apparatus is shown in Figures 3 and 4.



## GENERAL CHARACTERISTICS

The apparatus was designed to have an oxygen capacity of 100 cubic feet per hour of oxygen of 98 per cent purity, delivered continuously. The apparatus contained 120 pounds of 3-Methoxy Co-Ox which circulated once every fifteen to twenty minutes. The outside dimensions of the apparatus were 3 ft. x 2 ft. x 6 ft.

Electrical power was required; 220 volts direct current, 12 kilowatts if the deoxygenation was effected by electrically generated heat, 5 kilowatts if by steam heat. The input air flow was about 1,000 cubic feet per hour, the air being dried by passage through chambers containing 150 pounds of walnut potassium hydroxide and 35 pounds of anhydrous magnesium perchlorate.

The oxygenation chamber was constructed of 14 gauge spiral welded pipe, 12 inches in diameter and  $5\frac{1}{2}$  feet long. Refrigeration coils were soldered to the outside surface. It was covered with insulation 1 inch thick. The deoxygenation chamber was constructed of 14 gauge spiral welded pipe, 6 inches in diameter and  $5\frac{1}{2}$  feet long. It was heated electrically by chromel wire carried on porcelain insulators. The current was controlled by a 7.5 kilowatt variac, and for experimental purposes wattmeters were installed to measure the power consumption. Alternatively the deoxygenation chamber was heated by steam passing through a surrounding jacket. Water traps were provided to remove the water from the steam and catch the condensate for measurement. The compound in the chambers was stirred by narrow brass blades parallel to the axes of the chambers, carried on shafts supported on sealed ball bearings. These stirrers and the various other moving parts such as the augers in the transferring devices and the refrigerator compressor were powered by a 5 h.p. motor.

The refrigerant, Freon 12, was evaporated in seven parallel copper tubes,  $\frac{1}{2}$  inch in diameter soldered to the oxygenation chamber and the air cooler. The condenser of the refrigerator was cooled with water and was equipped with an automatic flow regulator; about 20 gallons of water per hour was used depending on the inlet temperature.

The compound was cooled to  $5^{\circ}$  in the oxygenation chamber and heated to  $80^{\circ}$  in the deoxygenation chamber. The specific heat of 3-Methoxy Co-Ox is 0.24 so that the heat to change 100 pounds of compound three times an hour through this temperature interval was 9,700 B.T.U. Using 20,000 cal. per g. mole of oxygen the heat of reaction was 14,300 B.T.U. per hour (mol. wt. of compound per mole of oxygen: 770). The total heat to be moved per hour was therefore 24,000 B.T.U. or 7.05 kw. Using 70 B.T.U. per hour per square foot as the applicable rate of heat transfer, and  $54.2^{\circ}$  as the average temperature gradient, the wall area needed for cooling the compound was 1.42 square feet. Using  $12^{\circ}$  as the temperature gradient during the oxygenation reaction, the wall area required was 9.74 square feet, giving a total wall area required of 10.2 square feet. The actual effective area was greater than this by about 20 per cent. Using  $100^{\circ}$  as the wall temperature of the deoxygenation chamber, the average temperature gradient during the heating was  $53.5^{\circ}$

and the wall area calculated to be 0.868 square foot. The temperature gradient during the deoxygenation reaction was  $20^{\circ}$  and the wall area required was 5.66 square feet. The actual effective area was considerably greater than the total area needed as calculated.

Based on these calculations, the apparatus shown in Figures 3 and 4 was designed and constructed. Numerous changes were made in various features of the apparatus during construction. The particularly difficult problems which arose are now discussed in detail followed by a description of the results obtained with the apparatus.

#### HEAT TRANSFER

Preliminary experiments indicated that if the 3-Methoxy Co-Ox were moved slowly through the chambers by means of slowly rotating augers, the contact of the material with the walls of the chambers was insufficient to yield the heat transfer needed. It was found that adequate heat transfer could be secured if the material were vigorously agitated. Heat transfer studies were made on specially designed auxiliary equipment to relate the heat transfer to the temperature gradient, to the speed of rotation of the stirrers used to agitate the material, to the character of the metal surface, and to other factors. Under favorable conditions a heat transfer rate of 75 B.T.U. per hour per square foot was obtained. This value was used in designing the apparatus and in actual operation this value was realized during the time that the chamber walls remained clean. After a period of operation, the walls became coated with a thick cake of compound.

#### MOVEMENT OF MATERIAL

The physical characteristics of 3-Methoxy Co-Ox when oxygenated and when deoxygenated differ greatly. The oxygenated material, black in color, acts like wet sand, packs easily, and does not flow readily. The deoxygenated material, maroon in color (when active), behaves like Portland cement, flowing as a liquid when disturbed. Under vigorous agitation both forms became suspended in the gaseous atmosphere and the suspension behaved much as a fluid. All of these characteristics had an effect upon the operation of the apparatus, movement of the suspended material occurring in the oxygenation and deoxygenation chambers and movement of the solid mass in the transferring devices. Suitable construction of the chambers, transferring devices, and the various augers, agitators, and dampers was found only after considerable experimentation. Numerous studies were made to find the most satisfactory pitch and speed of the augers in the transferring devices. A great deal of trouble was experienced with the damper used to control the flow of material through the apparatus; a satisfactory wedge shaped sliding damper of the proper dimension was finally found to answer. The suspended 3-Methoxy Co-Ox slowly made its way through the oxygenation and deoxygenation chambers by virtue of the agitation of the material while the material was

continuously added and withdrawn from opposite ends of each of the chambers. In the transferring device, the smooth flow and necessary compacting of the bed was secured only after repeated experimentation and redesign.

#### DUST FILTRATION

The high rate of agitation of the 3-Methoxy Co-Ox necessary to secure adequate heat transfer complicated the problem of filtering the finely divided 3-Methoxy Co-Ox from the air and oxygen streams. A bag type filter of cotton ticking supported on wire screen was found satisfactory and the dimensions of the filters as a function of the air flow were determined.

The amount of 3-Methoxy Co-Ox powder which reached the filter bags was minimized by replacing the agitator blades on the agitator directly below the filter bag house with several flights of screw conveyer. The augers kept the chambers emptied out at these points, and did not throw excessive powder into the filter bag house as the plain agitator blades had done.

#### TRANSFERRING DEVICES

The transferring devices introduced to transport the solid oxygen-carrying material from the oxygenation chamber to the deoxygenation chamber and back, and at the same time prevent the gases of the atmosphere of the two chambers from mixing, was simple in its fundamental idea but was difficult to reduce to practice. Some twenty devices were constructed to determine the best method of compacting and moving the solid material from one chamber to the other. In the final form the material was taken from the ends of the chambers and forced by means of a high speed, low pitch, horizontal auger into the bottom of a vertical standpipe in which it was forced to rise, forming a rather dense mass. The powder overflowed the vertical standpipe and slid down a chute into the other chamber. It was necessary to place a horizontal wire agitator in the vertical pipe to maintain the uniform flow of material through the entire cross section of the pipe and to maintain a satisfactory, gas pressure differential across the bed of material. The speed and pitch of the agitator, the pressure drop across the vertical pipe, the loss of oxygen diffusing through the bed, the efficiency of the removal of air from the material, the differences encountered at the hot and cold ends of the apparatus, and other difficulties which were finally overcome are too numerous to detail in this place.

#### REFRIGERATION OF THE OXYGENATION CHAMBER

The copper refrigerating coils were soldered directly to the outside of the oxygenation chamber. A study was made to determine the optimum length of the cooling coils and a detailed analysis was made of the operation of the refrigeration system to determine its efficiency and the heat actually removed during operation of the apparatus. A capacity booster was

placed on the system to increase the efficiency of the refrigerator and a heat exchanger was also installed to precool the air entering the oxygenation chamber. The refrigeration system functioned well, easily removing the 24,000 B.T.U. per hour of heat involved in the cooling and oxygenation.

#### OPERATION

After the various problems outlined above had been solved, a satisfactory mechanical operation of the apparatus was secured and an output of 80 cubic feet per hour of oxygen of 90 per cent purity was obtained. Heat balance and power consumption studies were made. On continued operation, however, the output of the apparatus gradually diminished, for example decreasing in one run from 80 to 20 cubic feet per hour in about six hours. This behavior was traced to the formation of an adherent coating of 3-Methoxy Co-Ox on the walls of the oxygenation chamber and the consequent decrease in the heat transfer. Moisture was not involved in the formation of this coating and the coating formed only after the crystals of 3-Methoxy Co-Ox were broken up by the continuous agitation taking place. The addition of foreign materials such as graphite and ferric oxide did not inhibit the formation of the coating. The only successful method of overcoming this difficulty appeared to be a system of mechanical scrapers which were engaged periodically to remove the coating. A suitable mechanical arrangement of scrapers was devised but never installed on the apparatus. The coating formed during the operation of the apparatus was extremely adherent, being removed with difficulty with hammer and chisel. The character of the surface has little to do with the formation of the coating and only slight pressure is required to cause the formation of an initial stain on the surface, after which the cake builds up rapidly. The formation of the cake is dependent only upon the peculiar nature of the oxygen-carrying material.

In a small auxiliary apparatus the deterioration of 3-Methoxy Co-Ox due to mechanical agitation alone was studied. In a dry, inert atmosphere at 100°, 3-Methoxy Co-Ox was inactivated by mechanical agitation in twenty hours, being converted to a bright red, inactive isomeric form. Unlike the corresponding inactive, bright red from the parent material (*see* Paper III), this inactive form could be reactivated by a brief heat treatment at 180°. The deterioration by agitation in the cold could not be determined, the adherent coating mentioned above being formed after a relatively few hours.

#### EXPLOSION HAZARD

The oxygen-carrying materials described in this series of papers are themselves not explosive, either in the oxygenated state or in the de-oxygenated state. Suspended in an atmosphere of oxygen they may, however, cause a dust explosion of some violence. A spark or highly heated surface is necessary to set off such an explosion. Two explosions did occur during the work on the circulating solid apparatus, one when welding was being done on the apparatus loaded with carrier and the

other during operation when the flow of material was stopped and the electrically heated deoxygenation chamber became overheated. Provision had been made for explosions, the filter housings having been provided with explosion heads of heavy, varnished paper which blew out easily. Flame accompanied the explosions. The explosions occurred in the oxygen filter housing and were confined to the material suspended in the filter housing or to a small amount opposite the hot welding spot, and possibly to a small amount acting as a fuse to the filter housing; the amount of material involved in the explosion was thus very small.

Further information on explosions was obtained with a pipe 6 inches in diameter and 8 inches long fitted with a two-bladed stirrer driven at 400 r.p.m. At one end of the pipe was placed a circular wooden stopper which would easily blow out in case of an explosion. The pipe was fitted with a small electric heating element to set off the explosion. The pipe was filled half full of compound and flushed with oxygen. With the stirrer running, the wire was then heated. The behavior was erratic; explosions sometimes occurred, but more frequently there occurred only a little puff followed by flame. Apparently the concentration of material in the atmosphere of oxygen was too high to cause an explosion. This was the situation in the deoxygenation chamber of the circulating solid apparatus. When the amount of material was reduced so that only a small amount was suspended in an atmosphere of oxygen an explosion was almost invariably obtained. A temperature of  $160^{\circ}$  was needed to set off such a mixture. No explosion could be made to take place when air was substituted for the oxygen. It was found that the explosion of the material suspended in oxygen could not be made to propagate through several layers of 16-mesh wire screen.

[ The present series of discussions of the "Studies on Oxygen-Carrying Cobalt Compounds" is concluded with this paper. ]

# EFFECT OF CORN SEED TREATED WITH TETRACHLORO-PARA-BENZOQUINONE ON THE GROWTH AND FATTENING OF SWINE

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A concerted effort was made during the war period by committees<sup>2</sup> of the American Phytopathological Society to encourage seedsmen to pre-treat seed before sale. This was the most practical method of bringing the benefits of seed treatment to the public without becoming involved in an extensive publicity campaign designed to change the practices of millions of farmers and home gardeners. The objectives of this program were entirely sound in that large volumes of seed could be treated by preferred methods with a minimum expenditure of labor and machinery and without requiring the large inventories of scarce fungicides necessary if seed treatment was left entirely to the agriculturists.

Although the seedsmen, in general, were receptive to this program, they were confronted with two serious obstacles. Treated seed could not be sent through the mail in ordinary containers, according to the postal regulations that were in force; and all surplus seed had to be destroyed because it could not be recommended for use as livestock feed. The first obstacle was quickly removed by securing a new ruling from the Postmaster General, who agreed to accept treated seed in simple, standard packets. The disposal of surplus treated seed was not so easily solved since it was necessary to demonstrate that the fungicidal treatments, as recommended, would have no ill effects upon the development of young animals or the fattening of feeders.

As a start on this problem, it was decided that tests should be made with tetrachloro-para-benzoquinone, since there was evidence (3) that it was relatively nontoxic to warm blooded animals and it had proved exceptionally effective as a seed protectant on peas (2,4,6,7,8), lima beans (1,5,7), corn (2,6,7), and other types of seeds. It was decided that treated corn seed would be used for feeding hogs, since swine can obtain practically all of their food concentrates from this crop. They also have relatively limited stomach capacity. The chemical would not

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<sup>1</sup> Formerly manager of Research and Development, Agricultural Chemicals Section, Naugatuck Chemical Division, United States Rubber Company. The author is deeply indebted to Dr. George Taylor, Dr. J. B. Skaptason, and L. F. Whitney, D.V.M., for technical advice, and to Arthur Russell, Alec Fenwick, and Max Rochelle for technical assistance in carrying out these experiments.

<sup>2</sup> Vegetable subcommittee of the Seed Treatment Committee and Fungicide subcommittee of the War Committee.

be diluted with a large volume of roughage as it would if fed to ruminants. Records on the growth, body characteristics, and food utilization of the animals receiving treated and untreated corn are reported in this article.

#### MATERIALS AND METHODS

The experiment was set up so there would be three lots of five animals each living under identical conditions (see Fig. 1) and having free access to food, minerals, and fresh water at all times. After the animals became adjusted to their environment and learned how to use the self-feeders,



FIG. 1. Arrangement of the feeding lots showing the identical facilities in each lot. At the time of this photograph, the subject in the foreground had been receiving Spergon-DDT-treated corn for 39 days; those in the center, Spergon-treated corn for 103 days; and those in the background, untreated corn for 103 days.

Lot A received normal corn; Lot B corn treated with Spergon (98 per cent tetrachloro-para-benzoquinone) throughout the period (117 days); and Lot C received untreated corn seed during the early growing period and Spergon-DDT (1.2 per cent DDT and 96 per cent tetrachloro-para-benzoquinone) treated feed during the last 53 days.

Good sound feed corn was purchased. Part of it was treated by conventional methods at the rate of 1.5 ounces per bushel. During the first three weeks it was ground into meal and thereafter it was cracked. The amount of chemical after the feed was processed was confirmed by a colorimetric analysis, so any deficit below the desired 0.16 per cent by weight, lost in milling, could be restored. During the last six weeks of the test suitable corn was not available on the market, so whole wheat was substituted.

In order to secure a homogeneous population for the experiment, an effort was made to obtain pigs of identical parentage and to be certain

they were growing uniformly before the test was started. It was necessary to locate two litters of pigs. Ones were chosen that had been farrowed within a day of each other and were by the same Chester White boar from half-sister Chester White-Poland China sows. Unfortunately, one pig was crushed before weaning so a substitution was necessary. These pigs were placed in adjacent lots of alfalfa pasturage 32' x 46' and provided with identical facilities (Fig. 1). The pigs were allocated to the three lots on the basis of weight, parentage, and sex so as to secure equal balance as shown in Table 1. The males were castrated and each animal

TABLE 1  
RECORDS ON HEREDITY, SEX, WEIGHT, AND GROWTH RATE OF TEST ANIMALS  
BEFORE STARTING EXPERIMENT

Test Subject			Weight of Animals				
Number Assigned	Sex	Litter	June 2	June 25	July 10	July 24	July 25
			(pounds)	(pounds)	(pounds)	(pounds)	(pounds)
A-70	Female	No. 1	18 5	39 6	61 5	77 1	77 0
A-71	Male	No. 1	8 9	25 6	41 3	53 9	54 3
A-72	Female	No. 2	14 9	32 5	50 5	61 2	62 4
A-73	Female	No. 2	15 3	34 6	52 5	67 5	67 2
A-74 *	Female	No. 3	11 1	19 6			
Totals			68 7	151 9	205 8	259 7	260 9
B-65	Male	No. 2	16 6	35 0	52 0	66 1	66 5
B-66	Female	No. 2	14 3	33 4	50 4	68 2	68 2
B-68	Female	No. 2	12 0	24 6	41 8	59 3	59 0
B-69	Female	No. 1	16 3	35 8	56 7	77 1	76 4
B-62 *	Female	No. 1	9 9	24 6			
Totals			69 1	153 4	200 9	270 7	270 1
C-61	Female	No. 1	15 8	32 6	53 2	73 4	72 5
C-63	Female	No. 2	12 5	30 0	47 9	63 8	63 0
C-64	Female	No. 2	19 3	42 8	61 7	78 2	77 8
C-67	Male	No. 1	15 1	31 8	48 2	65 9	65 3
C-60 *	Male	No. 2	9 4	27 0			
Totals			72 1	164 2	211 0	281 3	278 6

\* Removed because of poor growth rate.

was vaccinated, dewormed by phenothiazine, and carefully examined by Dr. Whitney, D.V.M. who pronounced them all sound and healthy.

The pigs were placed on a hog starter and skim milk diet for the first 23 days. During this period the gain in weight by pens, was A, 122 per cent; B, 122 per cent and C, 128 per cent; so the distribution seemed equitable. However, it was noticed that the substitute pig (A74) in the control pen was not growing as well as the other fourteen subjects, so she was eliminated. In order to keep the lots uniform, the poorest animal (B62 and C60) in each of the other pens was also removed.



During the next 15 days the four remaining pigs in the control Lot A gained 55.6 per cent; those in Lot B, 56.0 per cent; and those in Lot C, 53.8 per cent to give net gains of 73.5, 72.1 and 73.8 lbs., respectively. Obviously the three lots were as nearly identical as could be obtained with the available subjects.

In order to check food consumption from the equipment that was to be used in the ensuing experiment, identical self feeders, each with a compartment for grain and a smaller compartment for protein supplement, were placed in each pen. Both compartments were filled with starter mash and records were taken on consumption for the next 14 days. During this period, the aggregate weight per pen of four increased to 261, 270, and 279 pounds and 202.1, 210.8, and 227.3 pounds of feed were consumed respectively in the three pens. The gain per pound of feed consumed during this period was .375 pounds in Lot A, .302 in Lot B, and .323 in Lot C.

Obviously, the rates of growth and efficiency in utilization of food were almost identical. The starter ration then was removed, the grain compartments were filled with the appropriate type of corn meal, and the other compartment with a standard protein supplement. A separate supply of basic mineral and salt was maintained in each pen, fresh water was available at all times, and limited pasture was available until destroyed. Records were taken on the consumption of grain and supplement and the animals were weighed individually at regular intervals.

The animals were slaughtered when they reached a weight of approximately 220 pounds. Records were taken on the size and condition of internal organs and the viscera were carefully examined by a competent veterinarian.

## RESULTS OBTAINED

*Effect on growth.* The records on the weight of each animal from the time the experiment was begun on July 25, 1945, until they were slaughtered on November 19 are given in Table 2.

The significant fact in this experiment is that none of the pigs receiving treated grain were killed or showed any evidence of illness or lassitude. The rates of gain were identical in all three lots. The average weight per animal at the end of the experiment was 223.3 pounds in the control, 224.9 in the Sperguson-treated lot, and 220.8 in the Sperguson-DDT lot. These figures probably appear more nearly identical than they should since one of the control animals (A71) made atypical gain. Even if this animal and the poorest subject in Lot B were excluded from consideration, there would be less than six pounds difference in the average weight in the two pens; so there was no significant difference in weight. Apparently the chemical treatment had no effect on either the growth rate or fattening of the hogs. It is interesting to note that the average gain in weight per day was 1.29, 1.29, and 1.24 pounds per pig in the three lots—an excellent gain by commercial standards.

*Effect of food consumption.* There is little need to give a detailed record on the food consumption from week to week. There was no appreciable difference since Pen A consumed 2,536.9 pounds of corn; B, 2,302.4; and C, 2,408.2 pounds. The consumption of protein supplement was 258.4 pounds in Pen A, 378.6 pounds in Pen B, and 273.7 pounds in Pen C. There was a slightly heavier consumption of supplement in the lots receiving treated corn, particularly in the first three weeks after the treated seed was added. This observation suggests that treated seed was not quite so palatable as untreated, even though the taste was not

TABLE 2  
WEIGHTS OF SWINE ON DIFFERENT DATES DURING FEEDING EXPERIMENT

Animal * Tested	Weight of animals on different dates								
	Aug. 4	Aug. 18	Aug. 30	Sept. 20	Oct. 5	Oct. 24	Nov. 7	Nov. 12	Nov. 19
	(lb.)	(lb.)	(lb.)	(lb.)	(lb.)	(lb.)	(lb.)	(lb.)	(lb.)
A-70	92 2	114 5	129 7	160 6	183 5	205 7	227 7	234 6	241 2
A-71	69 0	90 7	103 0	122 7	144 6	161 2	175 3	181 3	183 9
A-72	78 7	96 7	114 4	145 3	170 1	198 0	224 5	228 3	235 7
A-73	81 5	103 7	119 7	146 9	165 4	191 3	216 1	224 1	232 7
Average	80 4	101 4	116 7	143 9	165 9	189 0	210 9	217 1	223 3
B-65	81 9	102 9	120 3	145 5	164 5	181 0	200 0	201 6	207 6
B-66	83 0	101 3	116 1	147 8	168 3	191 3	209 0	213 7	220 2
B-68	73 2	91 6	107 8	141 2	162 0	188 7	210 9	217 7	225 3
B-69	92 7	111 6	128 6	161 9	185 6	212 7	233 8	241 2	246 6
Average	82 7	101 8	118 2	149 1	170 1	193 4	213 4	218 6	224 9
C-61	85 8	104 8	118 1	143 5	165 6	192 1	205 8	217 3	223 5
C-63	76 9	97 7	112 2	145 0	168 7	200 9	213 8	215 2	222 0
C-64	90 8	109 1	121 3	145 2	167 4	191 4	205 3	210 0	220 0
C-67	80 3	103 8	115 4	138 9	164 8	187 8	202 3	217 1	217 5
Average	83 4	103 8	116 8	143 2	166 7	193 0	206 8	214 9	220 8

\* Animals in lot A received untreated corn. Those in lot B, Spergon-treated corn throughout, and those in lot C, Spergon-DDT-treated corn after September 27.

seriously objectionable to swine. The average consumption of all types of feed in the three lots was 5.728, 5.482, and 5.496 pounds per pig per day, respectively.

*The efficiency of the animals in converting feed into pork* was not affected by administering treated seed. Records on the amount of food consumed to produce a pound of gain are presented in Table 3.

*Effect on body and organ development.* When the animals were slaughtered, records were taken on the body weight before and after dressing, so that it was possible to calculate the dressing-out ratio (with heads on the carcass). All internal organs were weighed after draining and cooling. The records given in Table 4 show that there was no significant difference in internal organs except for an enlargement of the liver in the treated lots. These livers were considered normal by a veterinarian and histological sections failed to reveal any pathological condition.

TABLE 3  
AMOUNT OF TREATED AND UNTREATED FOOD REQUIRED TO PRODUCE A  
POUND OF GAIN IN BODY WEIGHT OF SWINE

Period of Observation Ending	Total Food Required to Gain 1 Pound		
	Untreated Check	Sperguson Treated	Sperguson-DDT Treated
	(pounds)	(pounds)	(pounds)
August 4. . . . .	3.49	3.55	3.89
August 18. . . . .	3.47	3.71	3.74
August 30. . . . .	3.61	3.61	3.89
September 20 . . . . .	3.80	3.61	3.90
October 5. . . . .	3.89	3.69	3.92
October 24. . . . .	4.11	3.92	4.05
November 7. . . . .	4.18	4.01	4.22
November 12. . . . .	4.23	4.05	4.22
November 19. . . . .	4.42	4.25	4.43

The animals in the control pen had a slightly better dressing percentage. Presumably, this was due to a shade better finish associated with a slightly heavier consumption of grain in the last two or three weeks of the experiment.

#### DISCUSSION

The significant fact uncovered in this test is that the fungicide did not cause any acute poisoning of the animals at the rate ordinarily used for treating seeds. None of the animals became ill, even though main-

TABLE 4  
DEVELOPMENT OF CARCASS AND INTERNAL ORGANS OF HOGS RECEIVING  
UNTREATED AND TREATED CORN

Animal Tested	Dressed Weight	Weight of Internal Organs			
		Heart	Liver	Lungs	Kidney
	(percentage)	(grams)	(grams)	(grams)	(grams)
A70. . . . .	78.3	259	1,210	946	293
A71. . . . .	76.3	273	1,864	1,092	285
A72. . . . .	80.5	248	1,590	854	257
A73. . . . .	77.7	260	1,621	630	280
Average. . . . .	78.3	260	1,571	880	279
B65. . . . .	79.3	217	2,388	664	246
B66. . . . .	75.6	263	2,121	1,052	243
B68. . . . .	75.8	259	2,389	1,275	265
B69. . . . .	75.4	318	2,157	920	332
Average. . . . .	76.5	264	2,264	978	272
C61. . . . .	76.2	241	2,081	495	292
C63. . . . .	78.8	280	1,343	1,431	275
C64. . . . .	78.0	270	2,051	806	234
C67. . . . .	76.2	230	2,298	1,086	261
Average. . . . .	77.3	255	1,941	955	266

tained on a steady diet of treated seed—a condition that would rarely be expected to hold on an average farm. These findings are entirely in keeping with the observations on laboratory animals made by McGavack *et al.* (3). They found an  $LD_{50}$  for rats by oral feeding of 4 grams per kilo of body weight. Translated to domestic animals, this would be equivalent to 4.8 pounds for a 1,200 pound steer or .8 of a pound for a 200 pound hog. They also observed that feed containing .044 grams daily apparently could be tolerated indefinitely (to 154 days) without causing appreciable injury.

It cannot be claimed that Spergon was absolutely inert when incorporated in the feed. In addition to reducing the animals' relish for the grain by a trifle, it did affect the liver. The 40 per cent enlargement is definite evidence of an unusual condition. It should be pointed out, however, that such an enlargement is not unusual in ordinary diets when used excessively—as, for example, when geese are force-fed. Although there was no evidence of tissue degeneration in the liver, it may be assumed that such could be expected if the dosage of tetrachloro-para-benzoquinone was multiplied several fold. McGavack *et al.* (3) found slight degeneration in about a third of the animals fed more than 0.3 per cent in feed. The rate used in this experiment was only half as much.

For all practical purposes, it can be said that seed treated with Spergon can be safely fed to swine. It is unlikely that under normal conditions animals will be subject to such a severe test as this one, where they were maintained on a full diet of treated corn throughout their growing and fattening period. It is possible that under some condition not encountered in this test, some injury from the fungicide might occur; but such a possibility is considered as rather remote. It is not logical at this time, however, to interpret these data as extending to every kind of domestic fowl and animal. Practical observations have been made, however, of cattle, chickens, and sheep receiving a few feedings of treated grain without deleterious effect.

#### SUMMARY

Corn seed treated with tetrachloro-para-benzoquinone at the rate ordinarily recommended (0.16 per cent by weight) as a seed protectant did not adversely affect either the growth rate or fattening of Chester White swine maintained on it continuously for 117 days. The animals grew at the same rate and made as efficient use of the food consumed as litter mates supplied with untreated seed from the same stock.

The use of seed treated with Spergon-DDT over a period of 53 days caused no adverse effects. The amount of food required to produce a pound of gain in body weight ranged from 3.5 to 4.4 pounds, depending upon the stage of development of the swine. At no time during the 117 days was there an appreciable difference in the food-growth ratio of the lots receiving treated and untreated seed.

The tetrachloro-para-benzoquinone apparently rendered the corn slightly less palatable, even though it did not interfere with normal con-

sumption of feed. The only other adverse effect detected was a moderate enlargement of the liver without creating any obvious pathological condition.

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# GROWTH OF THE YELLOW BASS, *MORONE INTERRUPTA* GILL, IN CLEAR LAKE, IOWA<sup>1</sup>

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Clear Lake, in Cerro Gordo County, is the third largest lake in Iowa and is one of the most important natural lakes in the state for fishing and recreational purposes. A scientific study of the fish population and fishery management problems of the lake was undertaken by the Iowa Cooperative Fishery Research Unit in 1941, 1942, and 1943. A brief description of the lake, a list of the species of fishes collected, and a discussion on certain ecological relationships of various fish species has already been published (Bailey and Harrison, 1945).

The present paper is concerned with the growth rate of one of the most important game fishes. Bailey and Harrison (1945, p. 69) state: "The yellow bass was introduced into Clear Lake, probably incidentally in mixed shipments of fish from the Mississippi River, and made its initial appearance in anglers' catches about 1932. The population increased rapidly so that except for the black bullhead it is now the most numerous pan or game fish in the lake." (See Fig. 1.)

## COLLECTION OF SAMPLES

Relative to the collection of fish, Bailey and Harrison state (p. 63): "A variety of gear was used in making collection, and no habitat was overlooked. Seines, ranging in length from 10 to 2,100 feet and in square-mesh size from 'common sense' to three inches, proved especially effective because most of the bottom is gently sloping and relatively free from impediments. Experimental gill nets with graduated mesh sizes from three-fourths to three inches were utilized in addition to standard nets of two, two and one-half, and four-inch square mesh. Many hook-and-line catches have been examined. The collections are distributed throughout the open-water season from April to November."

## LENGTH CONVERSION FACTORS

The length of a fish can be measured in a number of ways, depending

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<sup>2</sup> The authors wish to express their appreciation to Dr. Reeve M. Bailey and Mr. Harry M. Harrison, Jr. for permission to use the scale collections which form the basis of this paper. Dr. Bailey and Mr. Harrison collected, measured, weighed, and sexed the fish, collected the scales, and calculated the coefficients of condition.

upon the amount of the tail included in the measurement. In this growth study, standard length used in all calculations was measured in a straight line from the tip of the snout to the end of the hypural plate (base of the tail). In addition, total length, measured in a straight line from the tip of the snout to the tip of the caudal fin with the lobes of the fin compressed, was recorded for most of the fish. On the basis of the measurements on 290 yellow bass, the following conversion factors were calculated:

<i>To change</i>	<i>Multiply by</i>
Standard length to total length, no change in unit of measure .....	1.2451
Total length to standard length, no change in unit of measure.....	0.8031
Standard length in millimeters to total length in inches.....	0.0491
Total length in inches to standard length in millimeters.....	20.3987

No difference in these conversion factors was found between males and females, nor was there any evident change in the length of the tail with increase in length over the range of 160 to 259 millimeters.

#### SCALE PREPARATION AND PROJECTION

The scales were made ready for projection by placing the dry scales on a microscope slide, covering them with a few drops of water, and

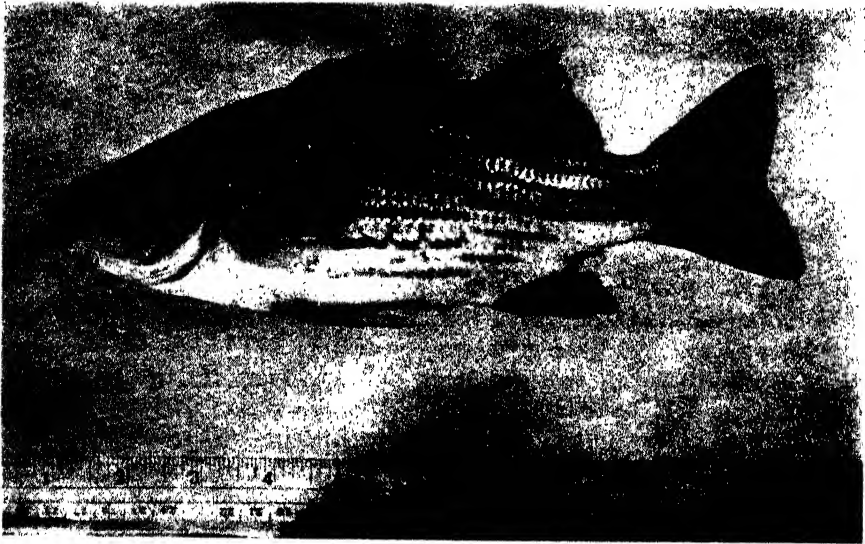


FIG. 1. Yellow bass from Cl ar Lake.

placing a second slide on top of them. Rubber bands were used to clamp the slides together and flatten the scales. A short time was allowed for the scales to become thoroughly wet, as it was found that the definition of the annuli was improved by this procedure. Projections were made with a microprojector similar to that described by Van Oosten, Deason, and Jobes (1934). A magnification of 27 diameters was used. The calculated growth at each annulus was determined with a nomograph (Carlander and Smith, 1944).

## BODY-SCALE RELATIONSHIP

In much of the earlier work on the calculation of growth rates from scale measurements, the body-scale relationship was assumed to be a straight line from zero, and the growth rates were calculated from the scale measurements by direct proportion. Recent studies have shown the necessity for determining the body-scale relationship for each species, and even for different populations of the same species. The body-scale

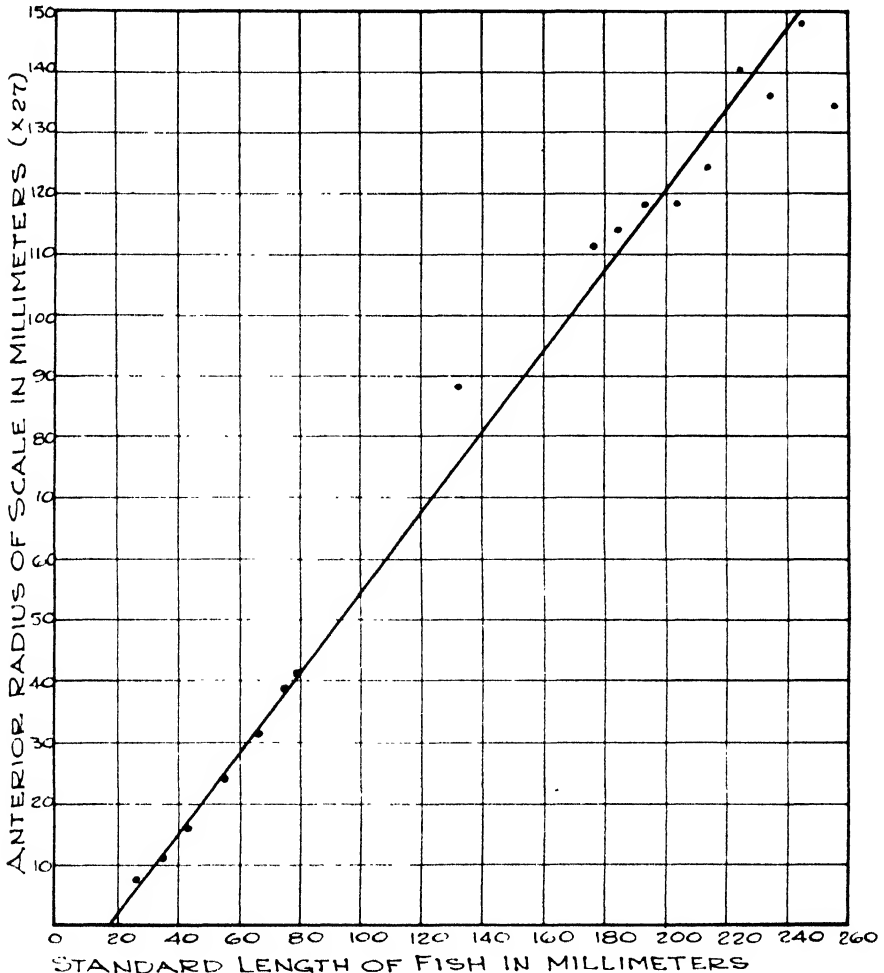


FIG. 2. Relationship between anterior radii of scales and standard lengths of Clear Lake yellow bass.

relationship of 396 yellow bass from Clear Lake (Fig. 2) was determined by plotting the mean body lengths at 10 millimeter intervals against the mean scale radii and fitting a straight line to the data by the least squares method. A straight line having a slope of 1.53 and an intercept on the



length axis of 16.2 millimeters fits the plotted data quite well. Therefore the growth calculations were made on a direct proportion basis using 16 millimeters as a base rather than zero (Carlander and Smith, 1944). Presumably, 16 millimeters is the length of the fish at the time the scales are formed.

#### VALIDITY OF SCALE METHOD

The scale method of age and growth determination has been used for a large number of species, but it is well to test the method whenever it is applied. The present study shows rather clearly that the annulus is a true year mark. As will be pointed out later, the great majority of the yellow bass collected in 1941, 1942, and 1943 belonged to the 1939 year-class. This predominant year class could be readily followed from year to year and the addition of a new annulus each year could be demonstrated. In 1941, the fish had two annuli; in 1942, three annuli; and in 1943, 4 annuli. The annuli of yellow bass are quite distinct and can be readily recognized, at least on the younger fishes. The comparison of calculated lengths for previous years, based on fish collected in different years of life, also serves as verification of the scale method.

#### GROWTH OF YOUNG-OF-THE-YEAR

Bailey and Harrison (1945) have already published a summary of some of the data given in Table 1. The data are given here in more

TABLE 1  
GROWTH OF YOUNG-OF-THE-YEAR CLASS

Collection Period	Number of Fish	Standard Length in Millimeters		Average Daily Growth for Period Between Collections
		Range	Mean	
July 25-Aug. 10, '42 . . . . .	44	32-56	42.2	
Sept. 2-Sept. 9, '42. . . . .	36	47-69	55.5	39 mm.
Nov. 5, '42. . . . .	41	52-82	61.9	10 mm.
July 10, '43. . . . .	216	22-34	28.5	
July 21-July 24, '43. . . . .	135	28-48	38.1	80 mm.
Oct. 29, '43. . . . .	58	52-82	65.0	27 mm.

detail, to present as complete a picture as possible of the growth of the young fish and to permit a comparison of the calculated growth for the first year of life with the actual measurements of the young-of-the-year. The rate of growth during the month of July appears to be more rapid than during the later months of the year. The 1943 yellow bass grew 0.8 millimeters per day for the period July 10 to 22.

The average calculated standard lengths for the first year of life for the 1937 and 1939 year classes were 91 and 84 millimeters, respectively (Tables 2 and 3). These calculated lengths are about 20 millimeters longer than the measured lengths of young-of-the-year yellow bass in late October, 1943, and early November, 1942. This difference between calculated and measured lengths may be the result of (1) further growth

TABLE 2  
CALCULATED AND MEASURED LENGTHS OF 13 YELLOW BASS OF THE  
1937 YEAR CLASS, SEXES COMBINED

Age Group	Number Examined	Standard Length in mm. at Time of Capture	Calculated Standard Lengths in mm. at the End of Each Year of Life				
			1	2	3	4	5
IV	3	237	95	178	209	227	
V	10	232	90	172	205	223	232
Total and means 13			91	173	206	224	232
Standard deviation of lengths			6 43	7 97	9 57	10 88	12 67
Equivalent total length in inches			4 47	8 49	10 11	11 00	11 39
Annual increment (mm. of S.L.)			91	82	33	18	8
Summation of annual increment			91	173	206	224	232

after the first of November but prior to annulus formation the next spring, (2) slower growth during 1942 and 1943 than in 1937 and 1939, or (3) discrepancies in body-scale relationship resulting in errors in calculated growth.

#### ABUNDANCE OF VARIOUS YEAR-CLASSES

The striking difference in the abundance of yellow bass hatched out in different years was noted by Bailey and Harrison (1945). They state (p. 69): "The strong 1939 year-class predominated in the catch from

TABLE 3  
CALCULATED AND MEASURED LENGTHS OF 277 YELLOW BASS OF THE  
1939 YEAR CLASS, SEXES COMBINED

Age Group	Number Examined	Standard Length in mm. at Time of Capture	Calculated Standard Lengths in mm. at the End of Each Year of Life			
			1	2	3	4
II	93	184	87	143		
III	159	190	82	138	180	
IV	25	210	88	148	187	203
Total and means 277			84	141	181	203
Standard deviation of lengths			8 57	9 36	7 44	9 07
Equivalent total length in inches			4 12	6 92	8 89	9 97
Annual increment (mm. of S.L.)			84	57	42	16
Summation of annual increment			84	141	183	199

1941 to 1944, at which time there was yet no evidence that it was losing its dominance." Bailey and Harrison found no young yellow bass of the 1940 year-class and only one of the 1941 year-class. In 1942 and 1943, however, they found many young yellow bass.

Out of the 290 fish over one year old examined in these growth studies, 13 were from the 1937 year-class and 277 were from the 1939 year-class. Apparently 1938, 1940, and 1941 were poor years for spawning or for survival of the young yellow bass. As yet, we have no indication of

the reasons for these poor years and good years, and this is one problem that needs further study. Similar, though usually less striking, differences in the abundance of fishes of various year classes have been reported for many other waters and other species of fishes.

#### GROWTH OF OLDER FISHES

The growth data on the 1937 and 1939 year-classes are kept separate since there is a considerable difference in the rate growth of the yellow bass in these two year classes (Tables 2 and 3). The fish in the 1937 year-class reached the Iowa legal length of seven inches, total length, during their second year of life, while the average yellow bass in the 1939

TABLE 4  
CALCULATED AND MEASURED LENGTHS OF CLEAR LAKE YELLOW BASS ARRANGED ACCORDING TO YEAR CLASS, COLLECTION DATE, AND SEX

Date of Collection	Age	Sex	No. of Fish	Calculated Standard Length (mm.) at End of Each Year Life					Standard Length (mm.) at Capture	
				1	2	3	4	5	Mean	Standard Deviation
(1939 Year Class)										
Sept. 23, 1941 . .	2	M	8	87	142				182	7.75
		F	21	91	148				188	7.82
Oct. 13, 1941	2	M	6	87	143				182	5.00
		F	6	86	142				185	3.75
Oct. 23-26, 1941	2	M	19	87	142				182	7.75
		F	7	86	145				186	6.48
Nov. 20, 1941 . .	2	M	15	82	141				183	6.15
		F	11	86	141				185	6.11
Apr. 29, 1942* .	3	M	28	85	143	184			184	7.06
		F	10	85	143	188			188	8.78
Oct. 1 & 3, 1942	3	M	52	81	137	177			190	8.01
		F	69	80	136	178			193	7.87
July 21-24, 1943	4	M	10	89	154	189	206		213	9.75
		F	12	89	146	186	202		208	7.32
Oct. 29, 1943 . .	4	F	3	80	138	182	199		208	8.56
(1937 Year Class)										
Oct. 28, 1941 . . .	4	M	3	95	178	209	227		237	6.37
Apr. 15 & 17, 1942* . . .	5	M	6	91	168	199	217	226	226	8.33
		F	4	90	176	213	232	242	242	9.75

\* Fish taken in the spring before the current annuli were laid down were classed as being one year older than the annulus count indicated. For fish of this category the calculated length for the last year of life is the same as the length at the time of capture.

year class did not reach this length until early in their third year. The annual increase in length was greatest during the first year of life for both year classes, and by the fourth year the average increase in length was fairly low.

In the above discussion, the growth data for males and females are combined, but Table 4 presents a breakdown of these data to show evidence of sexual differences in growth rates. During the first two years of life the males and females grow at the same rate, but in the third and fourth years the females appear to grow slightly more rapidly than the males. The difference is slight but an application of the  $t$  test to the average lengths at time of capture for the combined 1941 collections indicates that the difference is statistically significant ( $t = 3.01$ , probability 0.003). One is justified in combining the 1941 collections inasmuch as they were taken within a rather short period of time at the end of the growing season and show no evidence of growth during the period of collection.

The growth rate of yellow bass has been studied in a few other waters. A comparison of the average calculated lengths at various years of the Clear Lake yellow bass with those from Indiana and Tennessee waters indicates that the Clear Lake yellow bass are relatively fast growing (Table 5).

TABLE 5  
COMPARISON OF GROWTH IN LENGTH OF YELLOW BASS FROM VARIOUS LOCALITIES

Locality	Number of Fish	Calculated Total Length in Inches at End Each Year of Life					Authority
		1	2	3	4	5	
Clear Lake, Iowa							
1937 Year Class	13	4 5	8 5	10 1	11 0	11 4	Present Study
1939 Year Class	277	4 1	6 9	8 9	10 0		Present Study
Foots Pond, Indiana*	31	3 0	5 3	7 1	8 2	8 7	Ricker and
T.V.A. Reservoirs†	160	3 1	5 7	7 1	8 0	8 5	Lagler, 1942
							Stroud, 1947
Reelfoot Lake, Tennessee‡	129		7 8	8 7	10 0	11 6	Schoffman, 1940

\* Used straight line with origin at 20 mm. for body-scale relationships.

† Used straight line with origin at 0 mm. for body-scale relationship.

‡ Schoffman's values are not calculated lengths. They are mean measured lengths of fish of a given age collected during June, July, and August. The fish in the second year column are fish with one annulus and are in the second summer of growth, etc.

Yellow bass are apparently short-lived fishes. The oldest specimen taken in the present study was five years old and in its sixth year of growth. No older yellow bass were reported from other waters.

#### LENGTH-WEIGHT RELATIONSHIP AND COEFFICIENT OF CONDITION

It has been shown that the weight of fish increases approximately as the cube of the length. The length-weight relationship of 181 Clear

Lake yellow bass, covering a standard length range of 176 to 219 millimeters, was calculated by the least squares method:

$$W = 3.37 \cdot 10^{-4} L^{2.548}$$

or in logarithmic form

$$\text{Log } W = -3.47237 + 2.548 \text{ Log } L$$

where  $W$  = weight in grams

and  $L$  = standard length in millimeters.

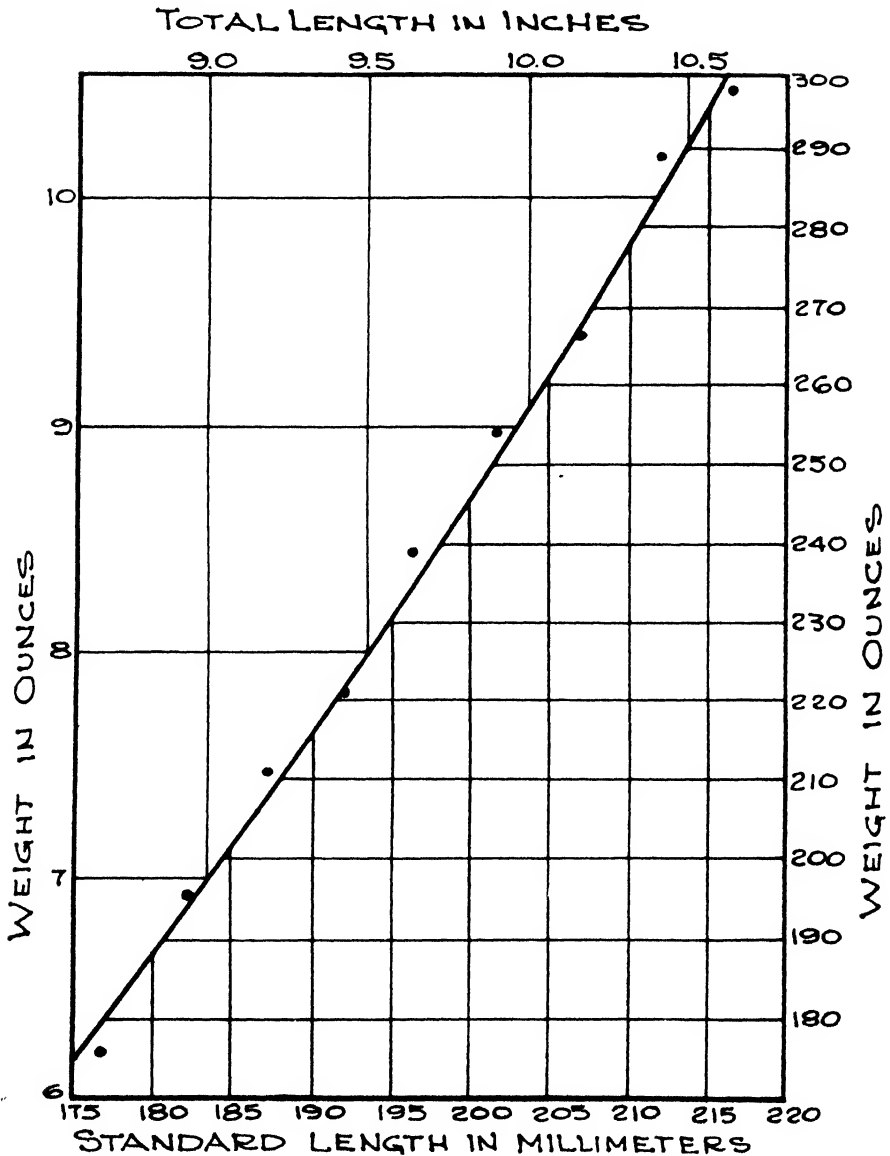


FIG. 3. Relationship between length and weight of Clear Lake yellow bass.

A comparison of the curve derived from this formula with the actual weights and lengths indicates a close agreement (Fig. 3).

By using this formula, the weights corresponding to the average calculated lengths at the end of each year may be determined. The yellow bass in the 1937 year class weighed 1.7, 6.0, 9.4, 11.6, and 12.7 ounces at the end of the first, second, third, fourth, and fifth years of life respectively, and the fish in the 1939 year class weighed 1.0, 3.7, 6.7, and 9.0 ounces at the end of their first, second, third, and fourth years. At the legal length of seven inches, the average yellow bass weighs about 3.8 ounces. It will be noted that although the greatest annual increase in length occurs in the first year of life, the greatest increase in weight is during the second or third year.

As an indicator of health, condition, or relative plumpness of fishes, a number of authors have used the coefficient of condition,  $K$ , where

$$K = \frac{W}{L^3} \cdot 10^5$$

if  $W$  = weight in grams

and  $L$  = standard length in millimeters.

The average  $K$  of 191 Clear Lake yellow bass was 3.18. The 1937 year class fish had higher  $K$  values than the 1939 year class, and prior to the spawning season the females usually were slightly plumper than the males (Table 6). Stroud (1947) listed 2.49 as the average  $K$  value

TABLE 6  
THE COEFFICIENT OF CONDITION,  $K$ , OF CLEAR LAKE YELLOW BASS

Year Class	Collection Date	Sex	Number	Range of $K$	Average $K$
1937	April, 1942	Male	6	3 18 3 66	3 44
		Female	4	3 17 4 18	3 67
1939	April, 1942	Male	28	2 82 3 57	3 12
		Female	10	3 03 3 47	3 26
	October, 1942	Male	52	2 60 3 53	3 15
		Female	69	2 84 3 77	3 23
	July, 1943	Male	10	2 72 3 26	2 98
		Female	12	2 83 3 06	2 94

of 141 yellow bass from T.V.A. waters, which indicates that the T.V.A. yellow bass are more slender than the Clear Lake yellow bass.

#### MANAGEMENT

Because of the dominance of certain year-classes in the yellow bass population and the almost complete lack of yellow bass in other year-classes, it can be anticipated that there will be years when the fishing for yellow bass will be exceptionally good and years when it may be poor. Since the yellow bass reach catchable size at the completion of the second

year or the beginning of the third, good fishing can be anticipated the second year after a dominant year-class hatches. The average fish caught will be fairly small during this year. If the year class was abundant, the fishing can be expected to hold up well the next year when the fish will be somewhat larger. Since the yellow bass put on most of their weight during the second or third year of life and since comparatively few live more than five years, the best utilization of these fish would be to catch them in their fourth and fifth years. The present size limit permits their capture during the third year of life while growth is still rapid. However, there is no evidence that the removal of these fish during the third year decreases the later catches. If further study indicates that a considerable portion of the fish are taken during their third year and that natural mortality is of little importance at this stage of life, it might be advisable to increase the size limit to 8 or 9 inches to provide better fishing in the fourth and fifth years when the yellow bass weigh over seven ounces. The fishing pressure should be heavy during these years so that the great majority of the fish are caught before the end of their natural life span.

Little is known of the causes of the differences in abundance of yellow bass in various year-classes, but these differences are probably the result of climatic or environmental conditions rather than of over-fishing. Further study may permit control of conditions to provide for greater survival of yellow bass in the poor years or of more frequent dominant year-classes.

The presence of dominant year-classes permits the prediction of fishing success a year or two in advance. If, for example, large numbers of year-old yellow bass are found in 1951, good fishing for small yellow bass can be anticipated in 1952, with large fish in 1953 and 1954. It may be desirable to regulate the fishing more stringently in years when poor year-classes are supporting the fishing, and to encourage and intensify the fishing when dominant year-classes are in the fourth and fifth years of life.

#### SUMMARY

1. The present paper reports on the growth rate of one of the most important fishes, the yellow bass, *Morone interrupta* Gill, in Clear Lake, Iowa.
2. In Clear Lake yellow bass, total length equals 1.2451 standard lengths.
3. The body-scale relationship, based upon 396 specimens over a wide range of sizes, gave a straight line with an origin at 16.2 millimeters standard length and a slope of 1.53.
4. The scale method appears valid for yellow bass. Annuli were added for each year of growth.
5. Growth of young-of-the-year yellow bass is most rapid during July. By the first of October young-of-the-year fish average 62 to 65 millimeters in standard length.
6. Most of the fish examined belonged to the 1939 year-class. A few

1937 year-class fish were examined and young fish were observed in 1942 and 1943. The 1938, 1940, and 1941 year-classes were very scarce, however.

7. The 1937 year-class yellow bass grew more rapidly than those in the 1939 year-class. The former reached legal length, 7 inches total length, during the second year of life while the latter did not attain this length until early in the third year.

8. Female yellow bass appear to grow slightly more rapidly than the males in the third and fourth years of life.

9. Comparison of the Clear Lake yellow bass data with that from other localities shows the Clear Lake yellow bass to be relatively fast growing.

10. The relationship between standard length ( $L$ ) in millimeters and weight ( $W$ ) in grams of the Clear Lake yellow bass can be expressed by the equation:

$$W = 3.37 \cdot 10^{-4} L^{2.548}$$

11. Although the annual growth in length is greatest during the first year of life, the greatest increase in weight occurs during the second or third year.

12. The average coefficient of condition,  $K$ , of 191 Clear Lake yellow bass was 3.18.

13. The dominance of certain year-classes will cause fluctuations in the success of fishing from year to year and may require periodic changes in management. Fishing should be heavy during those years in which dominant year-classes are four to five years old.

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# NOXIOUS WEED EXAMINATIONS — TIME SAVING METHODS

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Labor-saving devices and techniques are extremely welcome in a seed laboratory during the rush season. This has been particularly true the past few years since increased appreciation on the part of the public of the value of seed testing and the AAA program concerning the production of legume seed have seriously strained laboratory facilities during the winter and spring months.

## RAPID METHODS FOR NOXIOUS WEED SEED EXAMINATIONS

Several new techniques are quite effective in speeding up analysis of samples for noxious weed seed. Among these are the use of such devices as the Rice dodder mill for clover examinations, the use of a 1 mm. screen for timothy, and a special screening and blowing method for oats. A brief description of these methods and the benefits to be derived from each is presented below.

### 1. USE OF THE RICE DODDER MILL FOR NOXIOUS WEED EXAMINATION OF CLOVERS<sup>2</sup>

The laboratory model of this machine and its possible uses are familiar to most seed analysts; its value in cleaning impurities from small seeded legumes is self-evident. Whitcomb and Thompson<sup>3</sup> have recently published a short paper on the employment of a Rice dodder mill as a time saver in purity examinations. They found that most of the dirt, broken seeds, and weed seeds could be separated from a clover or alfalfa sample by running it through the machine, thus reducing subsequent workboard operations. Their data indicate that, on an average, about 10 minutes per sample were saved. The mechanism of the Rice dodder mill is adequately discussed by the above writers, hence a description will not be duplicated here.

Preliminary tests with the Rice cleaner indicated that the majority of the noxious weed seeds could be separated from clover and alfalfa samples in a fairly complete manner. Accordingly, the dodder mill was used experimentally to detect the presence of these seeds. It was

<sup>1</sup>Journal Paper No. J-1320 of the Iowa Agricultural Experiment Station, Ames, Iowa, Project No. 86.

<sup>2</sup>Assistance in various aspects of these experiments was given by Miss Georgena Wright and Mrs. Milliscent Buck. Helpful suggestions concerning the Rice dodder mill were given by Dr. R. H. Porter.

<sup>3</sup>W. O. Whitcomb and Bertha B. Thompson, "Analysis of seed with the Rice laboratory seed cleaner—preliminary tests." *Proc. A.O.S.A.* 34:70-72. 1942.

soon found that, with certain exceptions which will be discussed later, the presence or absence of noxious weed seeds in the small weed seed and dirt portion was an accurate index to their presence in the entire sample. Thus, examination of the large portion was necessary only when the presence of noxious weed seeds was indicated and an accurate numerical count desired.

The fact soon became apparent, as work with the machine progressed, that while different proportions of different weed seeds were separated from the clover, the proportion of any one kind removed was remarkably constant from sample to sample at any given speed of rotation of the rollers. This, of course, suggested a consideration of a possible quantitative as well as qualitative application of the seed cleaner.

Accordingly, a roller speed was determined which would give a good deposition of weed seeds without also throwing too large a proportion of the clover sample in the lower pan (the greater the speed of the rollers, the greater the amount of material dropped in the bottom tray). The rotation was finally set at 120 r.p.m. The handcrank with which the structure was originally provided was then removed and replaced by a constant-speed electric motor. A suitable wormgear provided the desired speed of rotation for the rollers.

Synthetic noxious weed examination samples, each containing 50 seeds of each of the noxious weeds, were prepared.<sup>1</sup> For some of the weeds, several samples were made up containing seeds from different sources; samples containing seeds of each of several species of dodder were also prepared.

Each sample was run through the Rice dodder mill fifty times. For each run, the weed seeds in the portion separated from the clover were counted and recorded, and on each third run the remainder of the bulk sample was checked through to be sure no weed seeds had been lost. The important thing in this operation is to control the flow of the sample so that it passes through the machine at a slow, uniform pace. If the seed is allowed to enter the mill rapidly, many of the weed seeds may "ride" through with the mass of clover seeds and never come in contact with the rollers; consequently, the percentage of weed seeds separated will not only be lowered but will be quite irregular. The rate of flow should be slow enough so that there will be no piling up—in order that every seed will have an adequate chance to come in contact with the rollers.

Among the Iowa noxious weeds, dock and buckhorn are much the most common in small seeded legumes. Quack grass, wild carrot, horse nettle, sheep sorrel, black mustard, and dodder (mostly in

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<sup>1</sup>The source of the weed seeds was (with the exception of perennial sow thistle, Russian knapweed, leafy spurge, and perennial peppergrass [too rare]) a supply saved from seeds removed from other samples during the course of routine testing. The surface of different weed seeds is variously affected by cleaning and threshing machinery; hence it is important that seeds from commercial samples be used rather than seeds harvested by hand.

alfalfa) are occasionally found; Canada thistle, wild mustard, and butterprint are of rather uncommon or rare occurrence. Perennial sow thistle, bindweed, leafy spurge, perennial peppergrass, and Russian knapweed are of such rare occurrence in Iowa clovers and alfalfa as to be best classed as novelties.

The results of above-described tests are tabulated in Table 1 for those weeds separating 75 per cent or better from the clover. Buck-horn plantain is the only weed seed at all common which is not in-

TABLE 1  
RESULTS ON WEED SEED RUNS THROUGH RICE DODDER MILL

Weeds	Percentage Separated	Factors
Perennial Sow Thistle ( <i>Sonchus arvensis</i> )	(Lot 1) 96 64 $\pm$ 2 56 (Lot 2) 97 44 $\pm$ 2 48	1 03
Canada Thistle ( <i>Cirsium arvense</i> )	(Lot 1) 95 44 $\pm$ 4 48 (Lot 2) 94 72 $\pm$ 4 50	1 05
Quack Grass . . . ( <i>Agropyron repens</i> )	(with lemma and palea) 92.66 $\pm$ 2 48 (caryopses) 95 84 $\pm$ 2 36	1 08 1 04
Dodder ( <i>Cuscuta</i> sp.)	(Lot 1) 85 90 $\pm$ 7 50 (Lot 2) 82 48 $\pm$ 6 56 (Lot 3) 88 26 $\pm$ 6 56	
Black Mustard ( <i>Brassica nigra</i> )	79 72 $\pm$ 6 16	1 25
Butterprint ( <i>Abutilon theophrasti</i> )	96 58 $\pm$ 3 68	1 04
Wild Carrot ( <i>Daucus carota</i> )	96 52 $\pm$ 2 16	1 04
Sour Dock ( <i>Rumex crispus</i> )	98 80 $\pm$ 2 09	1 01
Smooth Dock ( <i>Rumex altissimus</i> )	98 91 $\pm$ 1 88	1 01
Sheep Sorrel . . ( <i>Rumex acetosella</i> )	95 08 $\pm$ 2 66	1 05

cluded in this enumeration. The disposition of it and the other less common species will be discussed subsequently.

The data in the table include for each weed the mean percentage of seed separated for the fifty runs, the standard deviation of the individual tests, and factors for calculation of actual number of seeds present in the sample. The latter are merely the reciprocals of percentage separated.

If these results are to have application in routine testing, an interpretation in terms of noxious weeds tolerance is essential. The variability from test to test is, of course, the point under consideration.

It makes little difference whether the percentage of any given weed separated is 70 or 90; one need only multiply the number of seeds found by the appropriate factor to determine the total number in the sample, this being, in the example given above, the reciprocal of 0.7 or 0.9.

The best estimate of the applicability of these results would seem to be gained by comparing the expected variation with tolerances allowed, making use of the fact that variations over twice the standard deviation should not be expected at ordinary 0.05 odds.<sup>5</sup> The tolerance table for noxious weeds in the 1944 rules indicates that if 50 seeds are found by analysis, 37 will be within tolerance. Twice the standard deviation for 50 seeds is, of course, equal to the figures for a standard deviation percentage given in Table 1. Thus, for smooth and sour dock, with a possible variation of about 2, quack grass, wild carrot, sheep sorrel, perennial sow thistle, with a variation under 3, the variability against a tolerance of 13 would seem small enough to be disregarded. Variability of butterprint and black mustard is somewhat greater, but quantitative determination of these weed seeds may be justified. Dodder is not only more variable, but different species give somewhat different results. Probably the dodder mill should be used only as a detector for this weed seed, and a complete test should be made if it is found to be present.

The point can, of course, justifiably be made that the tolerance is set up to take care only of natural sampling variability and that such variation as is here discussed, whatever its size, merely adds that much to the chances of exceeding the tolerance. This is quite true. On the other hand, noxious weed examinations made by hand are by no means free from operational errors, especially when the sample contains a large number of seeds to be separated one after another. The elements of fatigue and natural human variability enter in, particularly when the pressure of work is great and the analyst must finish the sample rapidly with no chance to check over it again. Comparison of results obtained by hand analysis and a machine separation has indicated that, in many cases, more accurate results were obtained by the mechanical method with a considerably smaller expenditure of time.

Where the standard deviation does not exceed 5 per cent, such variation, for samples containing less than 10 seeds of any given nox-

<sup>5</sup> A statistical analysis to determine probability would seem to present considerable difficulty. The nature of the data indicates a binomial distribution, and it can be analyzed by the chi-square method in a fashion similar to that for germination and purity tests. Noxious weed tolerances are, however, based upon an assumption of a Poisson mode of distribution. The chi-square test will indicate considerably different probabilities for two weeds separated by the machine in proportions of 95 and 70 per cent, even though the variability of the individual test is equal. Such information has no application to the noxious weed tolerance problem and may be contradictory to practical considerations, i.e., dock, of which about 98 per cent of the seeds are separated with a standard deviation of only 2, presents a very low probability, while the very unsatisfactory separation of Russian knapweed, 31.3 per cent  $\pm 7.6$ , gives a probability of nearly 0.9.

ious weed, will only be fractional and of little significance. The fact that most of the factors given in the table exceed unity only slightly would lead one to expect that a complete separation would usually be effected in samples containing but few weed seeds. Experience has indicated that this is the case. As a matter of fact, in samples containing up to 20 dock or sheep sorrel seeds, complete separation is almost a certainty.

With respect to seeds of primary noxious weeds, it should be indicated that in Iowa and many other states the law prohibits the sale of crop seed containing any such seeds; hence, presence or absence of such seeds is the point of primary importance. While accuracy of numerical designation is desirable, this is a secondary consideration.

The chief problems relating to the practical application of the dodder mill for the detection of Iowa noxious weed seeds have to do with buckhorn plantain (*Plantago lanceolata*). The behavior of buckhorn seeds is variable from day to day, possibly due to the mucilaginous seed coat which becomes somewhat sticky on days when humidity is high. The seed coat, in any case, is smooth enough so that most of the seeds are deposited on the bottom pan with the clovers, and the chance of detection of the seed in the small separated portion is too small to be satisfactory. A special method has been devised to take care of this problem. The clover portion of the sample, on emergence from the machine, is caught in a sample pan. The person handling the machine quickly smoothes it out on the bottom of the pan (a small flattened stick has been found to be satisfactory for this operation) and looks it over. To a person trained in this operation the shiny seed coat of buckhorn stands out strongly against the clover and, if present, will be observed within 15 to 30 seconds time. To test the dependability of detection in this manner, a synthetic sample containing three buckhorn seeds was made up.<sup>a</sup> This sample was run through the machine a number of times, the large portion quickly examined as above described. The presence of buckhorn was detected in every case. This operation is facilitated by the fact that samples containing "good" buckhorn seed also contain immature, shriveled, or blackened seeds; the seed coats of the latter, being much more irregular and roughened than the good seeds, readily drop into the bottom portion where they may serve as indicators. Quantitative determination of buckhorn cannot be made in this manner; if its presence is noted, the entire sample should be examined on the workboard.

Horse nettle is separated from clover in a proportion of about 50 per cent; the figure is somewhat lower for wild mustard, perennial peppergrass, and Russian knapweed. Of these, horse nettle and wild mustard are the only ones common enough to be of much concern, and they may be detected by applying the double check method as

<sup>a</sup>This number was used because the provisions of the Iowa Seed Law require that buckhorn (a secondary noxious weed) be labeled in clovers, if present in numbers exceeding three per ounce.

described for buckhorn plantain. Perennial peppergrass is more likely to be missed than any of the others if it is present in small amounts. It was considered superfluous to make tests for bindweed, since it has not been observed in clover. If present, it would be conspicuous on account of its size and would doubtless be deposited in the weed separation because of its rough, warty surface.

Continual use of the Rice dodder mill tends to produce a certain amount of wear on the rollers which may change the exact percentage of a weed separated from the clover. If the machine is much used, it should probably be restandardized before each season's work.

It should be re-emphasized that this discussion has had reference only to weed seeds designated as noxious under the Iowa Seed Law. While many of these weeds are noxious in other states, others are likewise included. Many of the problems will probably have to be dealt with in a slightly different manner.

The Rice dodder mill has been used in the Iowa laboratory for purity tests in the manner discussed by Whitcomb and Thompson but only for "dirty" samples. The time saved on relatively well-cleaned samples does not appear to justify including this extra operation in the routine. However, if an analyst on weighing out a sample finds that it is dirty or weedy, the sample is set aside in a box provided for that purpose. After a few have accumulated, they are all run through the machine. The time saved on individual dirty samples treated in this manner ranged from ten minutes to three-quarters of an hour.

## 2. USE OF 1 MM. SCREEN FOR NOXIOUS WEED EXAMINATIONS OF TIMOTHY

If a timothy sample for noxious weed examination is shaken over a sieve possessing 1 mm. circular apertures, all of it will pass through quickly except a few unhulled grains. Among the Iowa noxious weeds, only two which occur with any frequency will pass through such a sieve; these are sheep sorrel and wild carrot.

The procedure used is as follows: The noxious weed seed portion is passed through the sieve, and only the remnants are examined on the workboard. If no noxious weed seeds are present, that fact is recorded on the work card; if, on the other hand, any weed seeds other than the above-mentioned pair are found, the number is determined and recorded. If either wild carrot or sheep sorrel seeds are found, it is necessary to go through the bulk sample as a certain proportion of these weed seeds has probably passed through the sieve and is mixed with the timothy.

A small amount of Canada thistle and perennial sow thistle will also pass through the sieve, but inasmuch as perennial sow thistle has not yet been found in Iowa timothy and Canada thistle is of rather rare occurrence, this fact will scarcely increase the percentage of samples in which bulk examination is necessary.

It is possible that adaptations of this method might be made for the seeds of weeds noxious in other states. Unfortunately this will probably

not be practical in many of the north-central states where oxeye daisy and yarrow are noxious, the seeds of these plants being small enough to pass readily through the screen with the timothy.

### 3. A SPECIAL METHOD FOR NOXIOUS WEED EXAMINATION OF OATS

An oat sample will be retained nearly in its entirety above an 8/64" buckwheat sieve (Seedburo 10B). The noxious weeds will, on the other hand, all pass through with the exception of butterprint, bindweed, and part of the quack grass. The presence of butterprint (occurring occasionally) and bindweed (very rare) can easily be determined by a quick examination of the bulk oat sample similar to that used for buckhorn in clovers. Quack grass, however, is not quickly discernible in oats and must be dealt with otherwise.

A larger blower, similar in general construction to the Iowa Air Blast Seed Separator, is used as an aid in purity examination of oats to blow out the empty glumes. The observation was made that such quack grass as occurred in these purity examinations was always separated from the main sample and blown up with the chaff. Accordingly, this fact was employed in the noxious weed examinations of oats.

During the rush season when several thousand samples of oats had to be disposed of in a relatively short period of time, an "assembly line" was set up as follows: One person was given the sole responsibility for dividing and weighing out the samples. The samples were passed on to another individual who operated the blower. The chaff was put into small envelopes and clipped to those containing the bulk samples. The next operator did the sieving, made a quick examination of the oats for butterprint and bindweed, and also looked over the material which passed through the sieve. If the sievings were small enough in amount so that one could easily see that no noxious weeds were present, or if such weeds (usually dock and mustard) were so few in number that they could easily be counted, these facts were noted. If, on the other hand, enough material had passed through the sieve so that the presence or number of noxious weeds was not readily observable, this material was added to the small envelope containing the blowings. The sample was then passed to the next person who, seated at a workboard, examined this small portion for quack grass, or other weeds if the sieved portion had been added to this sample. If the main bulk of the oat sample was observed to contain butterprint or bindweed, a complete examination of it was made on the workboard.

Noxious weed examinations have been given to upwards of three hundred oat samples in a 9-hour day by four people operating in the above manner.

### SUMMARY

Modified methods for noxious weed examination of small seeded legumes, timothy, and oats are presented. The suggested procedures, designed to reduce the amount of time used in noxious weed exam-



inations, are particularly recommended for testing for growers' information, farm sales, and other samples representing small lots. Seeds moving in interstate commerce should probably be tested in the regular manner in order to comply more exactly with the prescribed rules for seed testing.

A Rice dodder mill with a constant speed motor attachment is used for noxious weed examination of small seeded legumes such as clovers and alfalfa. Some noxious weeds, i.e., dock, wild carrot, quack grass, are separated in precise numerical proportions and may be directly determined quantitatively; others, buckhorn and dodders, are separated less precisely; for these the machine performs only a qualitative function. The noxious weed separation achieved by this machine, in addition to being much more rapid than that done by hand, in many cases is thought to be more accurate than the latter.

The modified method for timothy is based upon a separation of weed components and the crop by a 1 mm. screen. This is very successful for Iowa noxious weeds but may be less so in many other states.

The method suggested for oats is based on a combination of blowing (to remove quack grass) and separation with an 8/64" buckwheat sieve.

# THE DEVELOPMENT OF WAXY CORN FOR INDUSTRIAL USE<sup>1</sup>

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Cornstarch is the most important product produced from corn (*Zea mays* L.) by the wet-process milling industry. During the five-year period 1936-40, production averaged in excess of 900 million pounds per year exclusive of the cornstarch which is converted into dextrose, syrup, or dextrines. Domestic starches produced from materials other than corn averaged about 20 million pounds per year. In addition to this supply of domestic starch the United States, during this same period, imported, duty free, about 350 million pounds of tapioca and sago starch. "The annual consumption of 350 million pounds of tapioca in the world's largest cornstarch producing country may be attributed to two factors, price differential and the properties of the starch itself." (12)

Prior to World War II, most of the tapioca was imported from the Netherlands Indies, where labor is cheap and cassava tapioca (*Manihot esculenta* Crantz) produces large yields. Tapioca has been imported largely as tapioca flour, usually of poor quality, and is extracted after its arrival. From 1929 to 1939 the price of this low grade tapioca has averaged about one cent less per pound than that of cornstarch.

The quantities of tapioca required annually in the United States for special uses for which most other starches are not satisfactory have been estimated variously, from as low as 15 million pounds to as high as 200 million pounds.

Soon after the onset of World War II, tapioca importations dropped to practically nothing. In looking for tapioca substitutes it was shown that the starch from waxy corn had promising possibilities. As work progressed it became apparent that waxy cornstarch, while quite acceptable as a tapioca substitute, also had properties which enabled it to meet certain industrial requirements even better than high-grade tapioca starch. The chemical and genetic research with waxy corn and the history of its commercial expansion during the war years are reviewed briefly on the following pages.

A Presbyterian missionary in China, Rev. J. M. W. Farnham,

<sup>1</sup> Journal Paper No. J-968 of the Iowa Agricultural Experiment Station, Ames, Iowa, Project 616.

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observed an unusual type of corn prior to 1908. This type was recognized by the Chinese as having unusual characteristics and they had made some effort to propagate it in a pure condition. A sample of this corn was received from Reverend Farnham by the Office of Foreign Plant Introduction in March, 1908, and G. N. Collins made crosses to study its inheritance. The first report was published in 1909 (9) and the name "waxy" was suggested as being descriptive of its unusual endosperm texture. This and later reports (10,13) established that the gene conditioning waxy endosperm was inherited as a simple recessive. Following these early reports, the waxy gene *wx* has been used extensively in genetic studies.

Seven mutations from dent or flint endosperm types to waxy endosperm have been reported (1,2,4,5,15). Only one of these mutations resulted in the production of a new allele (2). The effect of this allele on starch properties will be discussed later.

In 1922 Weatherwax (17) and again in 1924 Brink and McGillivray (8) and Demerec (11) reported that waxy starch stained red or reddish brown with iodine, whereas ordinary starch stained a blue-black under similar conditions. Because of this staining property the starch was considered for a time to be an erythrodextrin. More recently it has been shown not to be a dextrin but amylopectin, a true starch.

Longley (14) also reported in 1924 that the waxy gene expresses itself in the pollen. Thus, in a heterozygous plant (*Wx wx*) approximately half of the pollen grains are red staining and half blue staining. The identification of heterozygous plants at the time of pollination by means of this differential staining has been an important factor in simplifying breeding operations.

In 1926, Brink (7) presented evidence that the starch from waxy corn differed in composition from common cornstarch. At that time starch chemistry had not progressed sufficiently to indicate the real difference between waxy cornstarch and common cornstarch.

In 1936, Dr. R. M. Hixon of the Plant Chemistry Department of Iowa State College milled experimentally one bushel quantities of dent, flint, pop, flour, sweet, and waxy corn. The amounts of starch obtained from the first five named types differed widely, but after the starch had been extracted was found to have similar chemical properties. The starch from the waxy corn, however, exhibited quite different physical and chemical properties. Waxy cornstarch pastes have higher viscosity and lesser rigidity than ordinary cornstarch pastes, and the shapes of the gelatinization curves differ for these two kinds of pastes. These properties of waxy cornstarch pastes resemble those of tapioca starch.

Chemically, waxy cornstarch differs from ordinary cornstarch in molecular structure. Starch from non-waxy corn is made up of a mixture of two molecular forms, straight chains and branched chains (3). The straight chain molecules represent the amylose fraction, and branched chain molecules the amylopectin fraction of ordinary cornstarch.

It is the straight chain component which is responsible for the blue staining reaction with iodine. The starch from the Chinese waxy corn has only the branched molecular form which stains reddish brown with iodine. Non-waxy cornstarch contains about 72 per cent branched chain and 28 per cent straight chain. The waxy allele reported by Andres (2) produces about 97 per cent branched chain and 3 per cent straight chain molecules.

Experiments have been reported (16) on the effects of various dosages of the waxy gene on starch properties. The materials used were Iowa 939 and Iowax No. 1. Iowa 939 was one of the first hybrids released by the Iowa Experiment Station and is homozygous starchy ( $WxWx$ ). Iowax No. 1 was produced by introducing the waxy gene into the four inbred lines involved in Iowa 939 by the backcrossing technic. Backcrossing was continued for several generations so that the lines  $I\ 205Wx$ ,  $I\ 205wx$  etc. should be largely isogenic. Four different endosperm genotypes were produced from these hybrids as follows:

1. Iowa 939 sib-pollinated . . . . .  $Wx\ Wx\ Wx$
2. Iowa 939 x Iowax No. 1 . . . . .  $Wx\ Wx\ wx$
3. Iowax No. 1 x Iowa 939 . . . . .  $wx\ wx\ Wx$
4. Iowax No. 1 sib-pollinated . . . . .  $wx\ wx\ wx$

Precautions were taken to insure that the four samples were handled similarly during milling and the subsequent starch characterization tests.

The relation between endosperm genotype and starch properties is illustrated in Table 1 and Figure 1.

TABLE 1.

THE RELATION BETWEEN ENDOSPERM GENOTYPE AND RIGIDITY AND VISCOSITY PROPERTIES OF THE ENDOSPERM STARCH

Starch No.	Genotype of Endosperm	Rigidity Dynes/cm. <sup>2</sup> × 10 <sup>-4</sup>	Viscosity in Centipoises	
			13 cm.	23 cm.
1.	$Wx\ Wx\ Wx$	22.2	24.1	16.5
2.	$Wx\ Wx\ wx$	18.5	41.8	25.8
3.	$wx\ wx\ Wx$	6.1	66.6	33.4
4.	$wx\ wx\ wx$	0	19.0	23.0

Sprague *et al.* (16) state that "although preliminary in nature, the foregoing results indicate that the waxy gene is not completely recessive in its influence as was previously believed. This is evidenced by the intermediate properties of the two heterozygous types,  $Wx\ Wx\ wx$  and  $wx\ wx\ Wx$ . Ignoring the completely recessive type,  $wx\ wx\ wx$ , the data on rigidity and viscosity indicate a simple additive type of factor action. The data on percentage amylose indicate a rather high degree of dominance.

"The fact that it is possible to produce starches of intermediate character is not of immediate industrial value because of the additional

expense which would be involved. For example, if it were desirable to produce a starch having viscosity and rigidity properties of the *Wx Wx wx* type, it would be necessary to produce the grain for milling in a detasseled crossing plot rather than in a regular commercial field."

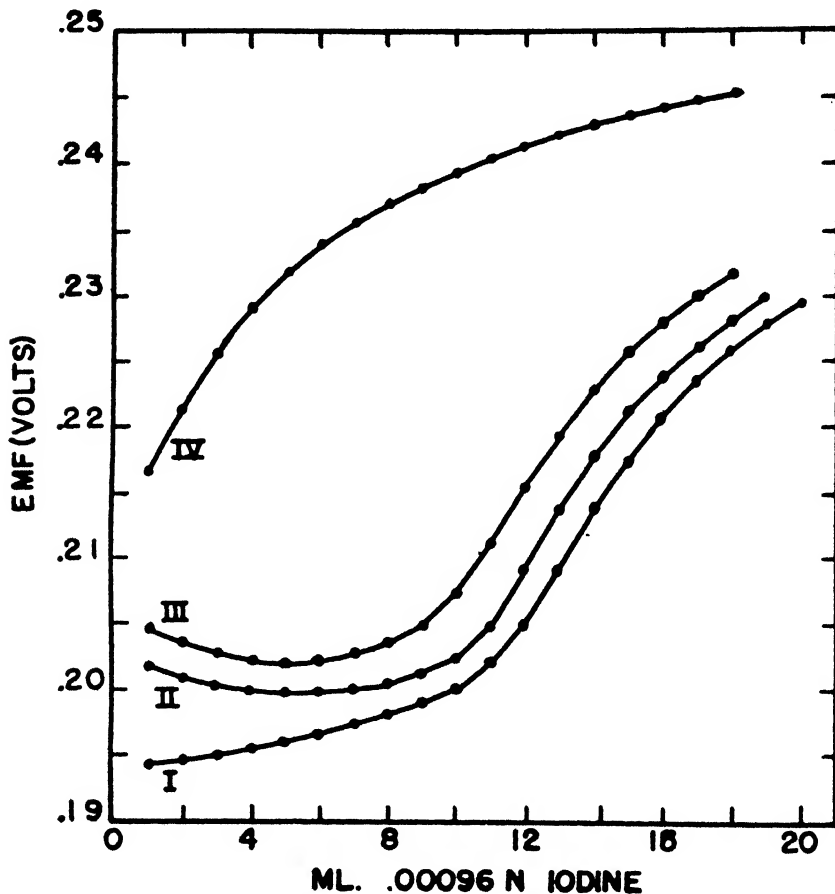


FIG. 1. Potentiometric curves for 0.04 per cent solution of starches. I, *Wx Wx Wx*; II, *Wx Wx wx*; III, *wx wx Wx*; IV, *wx wx wx*.

"The results promise to be of considerable theoretical interest, however, in studying the mechanism of starch synthesis in the kernel. They may provide an approach to the question of how the waxy allele promotes synthesis of starch made up entirely of branched molecules, while the starchy allele promotes synthesis of starch containing a mixture of straight and branched molecules."

A somewhat similar study was reported (6) using the Argentine

waxy mutant,  $wx^a$ , reported by Andres (2). By means of the sib pollinations and crosses it was possible to produce the following genetic types:

SERIES 1.	Iowax No. 1 sib-pollinated . . .	$wx\ wx\ wx$
	Iowax No. 1 x Argentine waxy . .	$wx\ wx\ wx^a$
	Argentine waxy x Iowax No. 1 . .	$wx^a\ wx^a\ wx$
SERIES 2.	Iowa 939 sib-pollinated . . .	$Wx\ Wx\ Wx$
	Iowa 939 x Argentine waxy . .	$Wx\ Wx\ wx^a$
	Argentine waxy x Iowa 939 . .	$wx^a\ wx^a\ Wx$
	Argentine waxy sib-pollinated . .	$wx^a\ wx^a\ wx^a$

The analytical results obtained are presented in Table 2 and Figure 2.

TABLE 2.

THE RELATION BETWEEN ENDOSPERM GENOTYPE, AMYLOSE PERCENTAGE, AND VISCOSITY OF THE ENDOSPERM STARCH

Genotype of Endosperm	Amylose Percentage	Viscosity Seconds (2 Per Cent Paste)
$wx\ wx\ wx$	0.0	65
$wx\ wx\ wx^a$	0.7	60
$wx^a\ wx^a\ wx$	1.3	42
$wx^a\ wx^a\ wx^a$	2.4	31
$Wx\ Wx\ Wx$	27.7	33
$Wx\ Wx\ wx^a$	27.4	52
$wx^a\ wx^a\ Wx$	26.7	78
$wx^a\ wx^a\ wx^a$	2.4	175

\* The viscosity measurements in the two halves of this table are not directly comparable as different sized capillary tubes were used.

Brimhall *et al.* (6) state that, "On the basis of loss of ability to synthesize amylose, this series of multiple alleles can be arranged in the order  $Wx$ ,  $wx^a$ , and  $wx$ . In this one respect  $Wx$  is dominant to both  $wx^a$  and  $wx$ . However, on the basis of viscosity measurements there is no clear indication of dominance. Considering only the  $wx^a$  and  $wx$  alleles, the variation in amylose percentage suggests a geometric and viscosity measurement an additive type of gene action. Genes which condition several effects, as measured by the end product, are said to be pleiotropic. Dominance relations may vary among the series of alleles depending on which of the manifold effects is chosen as the basis for classification.

"In the present case it appears that an assumption of pleiotropism may not be warranted. The three alleles  $Wx$ ,  $wx^a$ , and  $wx$ , affect the development of amylose and the amount of amylose present in the starch is reflected in its chemical and physical properties. Iodine-staining reaction, rigidity and viscosity measurements are merely different procedures for characterizing starch properties which may be differently influenced by amylose content. The apparent pleiotropism may be due entirely to the fact that none of these methods of characterizing starch provides a

complete delineation. Viscosity is a logarithmic function of starch concentration, while iodine titration is a linear function. Thus, very small differences in amylose content between  $Wx\ Wx\ wx^a$  and  $wx^a\ wx^a\ Wx$  might not be detected by iodine titration but would show up in viscosity determinations.

"The waxy cereals studied fall into two general groups. The first group characterized by starch lacking amylose, includes rice, sorghum, and corn ( $wx\ wx\ wx$ ). The second group, characterized by starch possessing a low percentage of amylose, includes barley and corn ( $wx^a\ wx^a\ wx^a$ ). The difference in iodine-staining reaction between waxy barley and other

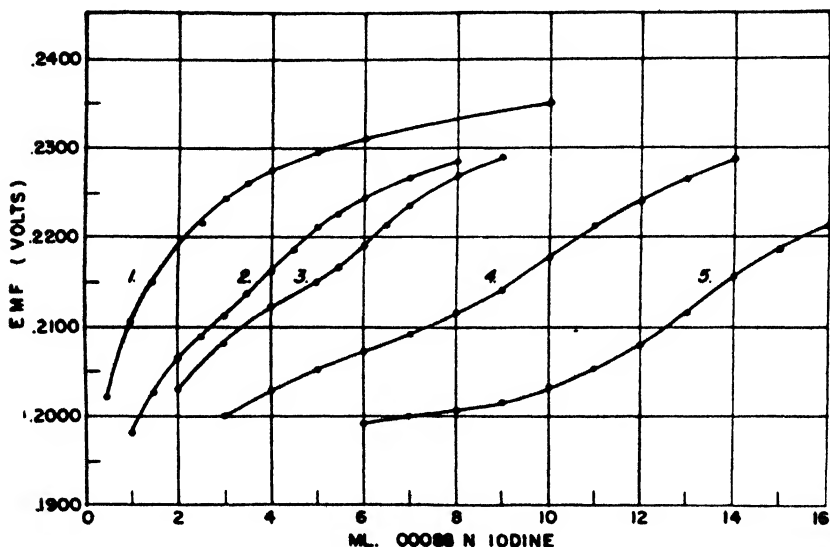


FIG. 2. Potentiometric titration curves for 0.02 per cent solutions of starches: 1,  $wx\ wx\ wx$ ; 2,  $wx\ wx\ wx^a$ ; 3,  $wx^a\ wx^a\ wx$ ; 4,  $wx^a\ wx^a\ wx^a$ ; 5, waxy barley.

waxy cereals has been noted (10), but a potentiometric iodine titration carried out at that time failed to detect the presence of amylose. This was undoubtedly due to the interference of fatty acids (0.33 per cent) in the barley starch. When this determination was repeated on a defatted sample, 3.5 per cent of amylose was found."

In view of the difference in physical and chemical properties of waxy cornstarch observed by Hixon in 1936, it was felt that waxy starch might have commercial possibilities. Available strains of waxy corn were not suited to commercial growing in the Corn Belt. Accordingly, a good commercial hybrid, Iowa 939, was chosen for conversion to the waxy condition. The four inbred parents were crossed with a waxy strain and then they each were recurrently backcrossed so as to completely recover their genotypes except for the addition of the waxy character. Later,

the process of converting numerous other standard non-waxy inbred lines to the waxy condition was inaugurated.

First agronomic tests of waxy Iowa 939, later known as Iowax No. 1, were begun in 1939. The yield of this hybrid was only slightly inferior to yields of its starchy counterpart. This slight reduction in yield may be characteristic of the waxy genotype. On ears segregating for both starchy and waxy kernels, the starchy kernels regularly weigh 3 to 5 per cent heavier than do the waxy kernels. This is about the same magnitude as the yield differences observed.

In the fall of 1941 when the Japanese invaded the islands of the Pacific, less than two bushels of seed were available of the waxy double-



FIG. 3. The first crossing block devoted to the commercial production of hybrid waxy corn.

cross hybrid, Iowax No. 1. Approximately 3,800 kernels were available of one of the parental singles, and 335 kernels of the other single-cross parent. There were also available limited quantities of seed of the four waxy inbred parents. In addition to this seed about 50 bushels of  $F_2$  seed were available from an isolated planting of Iowax No. 1, grown near Ames, Iowa.

In the winter of 1941-42 all of the available greenhouse space at Ames, Iowa, and Beltsville, Maryland, was used for advancing the two parent single-crosses to the  $F_2$  generation by sib-pollination. Sufficient  $F_2$  seed was obtained to plant a 20-acre double-crossing field in 1942 (Fig. 3) and an additional 20 acres of isolated increase fields of the parental single crosses.

The major portion of the available inbred seed was used to produce single crosses. The 50 bushels of  $F_2$  seed of the double cross Iowax No. 1 was used to plant 326 acres on College Farm land. The resulting crop was milled and produced about 500,000 pounds of waxy cornstarch.

Approximately 450 bushels of double-crossed seed were obtained in



1942. A part of this was of rather poor quality due to the use of  $F_2$  seed, and only 250 bushels, enough to plant 1,750 acres, was used in 1943. Sufficient  $F_1$  single-cross seed was available in 1943 to plant the required acreage of double-crossing blocks. By 1944 the acreage of waxy corn had increased to 10,000 acres, and by 1946 there were approximately 20,000 acres of waxy corn being grown.

In the period from 1941 to 1946 several new waxy double crosses were developed and tested. Three of the new hybrids were grown commercially in 1947. Iowax No. 1 has been replaced by Iowax No. 2, and limited quantities of Iowax 5 and 6 will also be used. Each of these hybrids is superior to Iowax No. 1 in yielding ability and other agronomic characters.

The commercial use of waxy corn hybrids has necessitated modifying the policies on the release and distribution of inbred lines previously followed by the Iowa Agricultural Experiment Station. The various waxy lines are phenotypically indistinguishable from their starchy counterparts with the exception of their reaction to iodine. It was felt that the release of such lines might result in confusion in the hands of the seed producers to the detriment of both the starchy and waxy hybrids. Consequently, it was decided not to release the waxy lines. This policy required that some provision be made for the production of the necessary quantities of single- and double-cross seed.

The Experiment Station, through its Committee for Agricultural Development, has a continuing contract with the American Maize-Products Company to produce whatever quantity of seed is deemed necessary. This waxy seed has been sold to the American Maize-Products Company at the prevailing price for standard double-cross hybrids.

The commercial production of waxy corn requires very careful supervision. The entire acreage is grown under contract, and a certain amount of canvassing is necessary to obtain the contract acreage. Each field must be inspected prior to harvest to determine whether contamination by foreign pollen has exceeded the tolerance limit, (5 per cent). In the beginning it was felt that pollen contamination would be a serious difficulty in the production of a high-quality starch, but four years' experience has indicated that such contamination is a minor problem.

In general, the milling companies are not equipped with storage space for large quantities of corn. This requires that there be some supervision of the shipping of the waxy corn to insure a sufficient volume for a continuous grind.

The Iowa Agricultural Experiment Station has felt that these various supervisory functions could not be undertaken as a part of its regular duties. Beginning in 1943, therefore, the American Maize-Products Company has contracted with the Doane Agricultural Service, a farm management and land appraisal concern, to act as its field representative in supervising the production and marketing of the crop.

Waxy corn is a premium crop. Farmers who grow this crop receive a premium of 12 per cent above the market price for ordinary corn. In

general, the farmers are well satisfied with the crop and the price received for it. Waxy cornstarch has met with ready acceptance by the industrial users, and the breeding program is being continued on the assumption that waxy corn will have a permanent place in the agriculture of the Corn Belt.

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# A LIST OF GENERALIZED LAPLACE TRANSFORMS<sup>1</sup>

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If a function  $F(x)$  may be expanded as a Newton series,

$$(1) \quad F(x) = \sum_{n=0}^{\infty} \Delta^n F(0) \binom{x}{n},$$

where  $\Delta F(x) = (E - 1)F(x) = F(x + 1) - F(x)$ , Milne-Thomson [1] has defined the generating function  $f(s)$  by the infinite series

$$(2) \quad f(s) = \sum_{n=0}^{\infty} \frac{F(n)}{s^{n+1}}.$$

Jordan [2] and Samuelson [3] have outlined the application of (2) to the solution of systems of difference equations [4]; the latter has stressed the generalized nature of the operations defined by infinite sums and the relations between them and the classical integral transformations. The generalized Laplace transformation is defined as

$$(3) \quad L \{F(k)\}_E = f(s) = \sum_{n=0}^{\infty} \frac{F(n)}{s^{n+1}},$$

where  $E$  is the shifting operator defined above and  $k$  is integral. It may be shown that any function  $F(k)$  will possess a generalized Laplace transform if it is of exponential order,  $|F(k)| \leq M a^k$ ,  $k > K$ , and is defined at all integral values of  $k$ . The parameter  $s$  in (3) may be real or complex, the series will converge uniformly for  $s \geq a_0 > a$ , and

$$\lim_{s \rightarrow \infty} f(s) = 0$$

<sup>1</sup>This paper is part of the thesis submitted to the Graduate Faculty of Iowa State College in partial fulfillment of the degree of Doctor of Philosophy, under the direction of Prof. H. P. Thielman.

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A system of difference equations may be transformed to an algebraic or differential system by the formulas

$$(4) \quad L \left\{ E^m F(k) \right\}_E = s^m f(s) - \sum_{j=0}^{m-1} s^{m-1-j} F(j) ,$$

$$(5) \quad L \left\{ \Delta^m F(k) \right\}_E = (s-1)^m f(s) - \sum_{j=0}^{m-1} (s-1)^{m-1-j} \Delta^j F(0) ,$$

$$(6) \quad L \left\{ k^{(m)} F(k) \right\}_E = \left( -\frac{d}{ds} \right)^m s^m f(s) ,$$

$$(7) \quad L \left\{ (k+1)^{- (m)} F(k) \right\}_E = (-s)^m \left( \frac{d}{ds} \right)^m f(s) ,$$

where  $k^{(m)} = k(k-1) \dots (k-m+1)$  and  $(k+1)^{- (m)} = (k+1)(k+2) \dots (k+m)$ , the so-called factorial polynomials. The inverse transformation may be effected by the use of the table of transforms of this paper. Some other properties which follow from the definition (3) are

$$(8) \quad L \left\{ a^{k+1} F(k) \right\}_E = f\left(\frac{s}{a}\right) ,$$

$$(9) \quad L \left\{ \sum_{n=0}^{k-1} F(n) \right\}_E = \frac{1}{s-1} f(s) ,$$

$$(10) \quad L \left\{ \frac{F(k)}{k+m} \right\}_E = s^{m-1} \int_s^\infty \frac{1}{x^m} f(x) dx ,$$

$$(11) \quad \sum_{n=0}^\infty \frac{F(n)}{n+m} = \int_1^\infty \frac{1}{x^m} f(x) dx .$$

In (10) and (11)  $m$  need not be an integer and it is understood that both infinite sum and infinite integral are to be convergent.

Two other methods of evaluating the inverse transformation are convolution and real or complex inversion. Multiplication together of the two series which define the two transforms  $f(s)$  and  $g(s)$  lead to the convolution theorem

$$\begin{aligned}
 (12) \quad f(s)g(s) &= L \left\{ \sum_{n=0}^{k-1} F(k-1-n)G(n) \right\}_E \\
 &= L \left\{ \bar{F}(k) \overset{E}{*} G(k) \right\}_E .
 \end{aligned}$$

The method of real inversion follows at once from the process of finding the coefficients of the Taylor series,

$$(13) \quad \bar{F}(k) = \frac{1}{k!} \left( \frac{d}{ds} \right)^k \left[ \frac{1}{s} f\left(\frac{1}{s}\right) \right]_{s=0} ,$$

while Cauchy's integral formula [5] leads at once to the complex inversion integral,

$$(14) \quad \bar{F}(k) = \frac{1}{2\pi i} \int_C z^k f(z) dz ,$$

where the simple closed curve  $C$  encloses the singular points of  $z^k f(z)$ . Finally,

$$(15) \quad \bar{F}(k) = \text{Sum of the residues of } z^k f(z) \text{ at the singular points enclosed by the curve } C.$$

As an example of the application of the generalized Laplace transformation to a problem in finite differences consider the integral

$$(16) \quad F(n) = \int_0^\infty e^{-px} x^n \cos qx \, dx .$$

Integration by parts yields the difference equation

$$(17) \quad (p^2 + q^2) F(n) - 2np F(n-1) + n(n-1) F(n-2) = 0 ,$$

which may be changed by the substitution  $F(n) = n! U(n)$  to

$$(18) \quad U(n+2) - \frac{2p}{p^2 + q^2} U(n+1) + \frac{1}{2} U(n) = 0 .$$

The boundary conditions are

$$(19) \quad U(0) = \frac{p}{p^2 + q^2} \quad \text{and} \quad U(1) = \frac{p^2 - q^2}{(p^2 + q^2)^2};$$

application of (4) to (18) yields the transform

$$(20) \quad u(s) = \frac{p}{p^2 + q^2} \frac{s - \frac{1}{p}}{s^2 - \frac{2ps}{p^2 + q^2} + \frac{1}{p^2 + q^2}},$$

which may be written in the form

$$(21) \quad u(s) = \frac{p}{p^2 + q^2} \frac{s - \frac{p}{p^2 + q^2} - \frac{q}{p} \frac{q}{p^2 + q^2}}{s^2 - \frac{2ps}{p^2 + q^2} + \frac{1}{p^2 + q^2}}.$$

If  $\cos w = \frac{p}{\sqrt{p^2 + q^2}}$ ,  $\sin w = \frac{q}{\sqrt{p^2 + q^2}}$ ,  $a = \frac{1}{\sqrt{p^2 + q^2}}$ , then by means

of (4) and (5) in the list of transforms the inversion of (21) leads to the final form of the solution of the difference equation (17),

$$(22) \quad F(n) = n! \left( \frac{1}{p^2 + q^2} \right)^{\frac{n+2}{2}} \left[ p \cos nw - q \sin nw \right].$$

TABLE OF TRANSFORMS

	$F(k)$	$f(s)$
1.	1	$\frac{1}{s-1}$
2.	$a^k$	$\frac{1}{s-a}$
3.	$a^{k-n} \binom{n}{k}$	$\frac{n!}{(s-a)^{n+1}}$
4.	$a^k \sin wk$	$\frac{a \sin w}{s^2 - 2as \cos w + a^2}$
5.	$a^k \cos wk$	$\frac{s - a \cos w}{s^2 - 2as \cos w + a^2}$
6.	$a^k \sinh wk$	$\frac{a \sinh w}{s^2 - 2as \cosh w + a^2}$
7.	$a^k \cosh wk$	$\frac{s - a \cosh w}{s^2 - 2as \cosh w + a^2}$
8.	$a^k \sin \frac{\pi}{2} k$	$\frac{a}{s^2 + a^2}$
9.	$a^k \cos \frac{\pi}{2} k$	$\frac{s}{s^2 + a^2}$
10.	$a^k \frac{1 - \cos \pi k}{2}$	$\frac{a}{s^2 - a^2}$
11.	$a^k \frac{1 + \cos \pi k}{2}$	$\frac{s}{s^2 - a^2}$
12.	$a^{k-n+p} \sum_{i=0}^p \binom{p}{i} \frac{k^{(n+1-p)}}{(n+1-p)!}$	$\frac{s^p}{(s-a)^{n+1}}$



13.  $\frac{a^k - b^k}{a-b}$   $\frac{1}{(s-a)(s-b)}$
14.  $\frac{a^{k+1} - b^{k+1}}{a-b}$   $\frac{s}{(s-a)(s-b)}$
15.  $\frac{a^k}{(a-b)(a-o)} + \frac{b^k}{(b-a)(b-o)} + \frac{o^k}{(o-a)(o-b)}$   $\frac{1}{(s-a)(s-b)(s-o)}$
16.  $\frac{a^{k+1}}{(a-b)(a-o)} + \frac{b^{k+1}}{(b-a)(b-o)} + \frac{o^{k+1}}{(o-a)(o-b)}$   $\frac{s}{(s-a)(s-b)(s-o)}$
17.  $\frac{a^{k+2}}{(a-b)(a-o)} + \frac{b^{k+2}}{(b-a)(b-o)} + \frac{o^{k+2}}{(o-a)(o-b)}$   $\frac{s^2}{(s-a)(s-b)(s-o)}$
18.  $a^k \left[ \cos \pi k - 2 \cos \frac{\pi}{3}(k+1) \right]$   $\frac{3a^2}{s^3 + a^3}$
19.  $a^k \left[ \cos \pi(k+1) - 2 \cos \frac{\pi}{3}(k+2) \right]$   $\frac{3as}{s^3 + a^3}$
20.  $a^k \left[ \cos \pi k + 2 \cos \frac{\pi}{3}k \right]$   $\frac{3s^2}{s^3 + a^3}$
21.  $-(k-1) a^k \sin \frac{\pi}{2}k$   $\frac{2a^3}{(s^2 + a^2)^2}$
22.  $-k a^k \cos \frac{\pi}{2}k$   $\frac{2a^2s}{(s^2 + a^2)^2}$
23.  $(k+1) a^k \sin \frac{\pi}{2}k$   $\frac{2as^2}{(s^2 + a^2)^2}$
24.  $(k+2) a^k \cos \frac{\pi}{2}k$   $\frac{2s^3}{(s^2 + a^2)^2}$
25.  $(k-1) a^k \frac{1 - \cos \pi k}{2}$   $\frac{2a^3}{(s^2 - a^2)^2}$

$$26. \quad k a^k \frac{1 + \cos \pi k}{2} \qquad \frac{2 a^2 s}{(s^2 - a^2)^2}$$

$$27. \quad (k+1) a^k \frac{1 - \cos \pi k}{2} \qquad \frac{2 a s^2}{(s^2 - a^2)^2}$$

$$28. \quad (k+2) a^k \frac{1 + \cos \pi k}{2} \qquad \frac{2 s^3}{(s^2 - a^2)^2}$$

$$29. \quad k a^k \sin \pi k \qquad \frac{a \sin w (s^2 - a^2)}{(s^2 - 2 a s \cos w + a^2)^2}$$

$$30. \quad k a^k \cos \pi k \qquad \frac{a \cos w (s^2 + a^2) - 2 a^2 s}{(s^2 - 2 a s \cos w + a^2)^2}$$

$$31. \quad - \sin \frac{\pi}{2} k \sum_{i=0}^{\infty} \binom{\frac{k-1}{2}}{2i+1} a^{k-3-4i} (a^4 - b^4)^i \qquad \frac{1}{s^4 + 2 a^2 s^2 + b^4}$$

$$32. \quad - \cos \frac{\pi}{2} k \sum_{i=0}^{\infty} \binom{\frac{k}{2}}{2i+1} a^{k-2-4i} (a^4 - b^4)^i \qquad \frac{s}{s^4 + 2 a^2 s^2 + b^4}$$

$$33. \quad \sin \frac{\pi}{2} k \sum_{i=0}^{\infty} \binom{\frac{k+1}{2}}{2i+1} a^{k-1-4i} (a^4 - b^4)^i \qquad \frac{s^2}{s^4 + 2 a^2 s^2 + b^4}$$

$$34. \quad \cos \frac{\pi}{2} k \sum_{i=0}^{\infty} \binom{\frac{k+2}{2}}{2i+1} a^{k-4i} (a^4 - b^4)^i \qquad \frac{s^3}{s^4 + 2 a^2 s^2 + b^4}$$

$$35. \quad - a^k \cos \frac{\pi}{4} (k+1) \frac{1 - \cos \pi k}{2} \qquad \frac{a^3}{s^4 + a^4}$$

$$36. \quad a^k \sin \frac{\pi}{4} k \frac{1 + \cos \pi k}{2} \qquad \frac{a^2 s}{s^4 + a^4}$$

$$37. \quad a^k \sin \frac{\pi}{4} (k+1) \frac{1 - \cos \pi k}{2} \qquad \frac{a s^2}{s^4 + a^4}$$

38.  $a^k \cos \frac{\pi}{4} k \frac{1 + \cos \pi k}{2}$   $\frac{s^3}{s^4 + a^4}$
39.  $a^k \left[ \frac{1 - \cos \pi k}{2} - \sin \frac{\pi}{2} k \right]$   $\frac{2s^3}{s^4 - a^4}$
40.  $a^k \left[ \frac{1 + \cos \pi k}{2} - \cos \frac{\pi}{2} k \right]$   $\frac{2s^2}{s^4 - a^4}$
41.  $a^k \left[ \frac{1 - \cos \pi k}{2} + \sin \frac{\pi}{2} k \right]$   $\frac{2as^2}{s^4 - a^4}$
42.  $a^k \left[ \frac{1 + \cos \pi k}{2} + \cos \frac{\pi}{2} k \right]$   $\frac{2s^3}{s^4 - a^4}$
43.  $\frac{a^k}{k!}$   $\frac{1}{s} e^{\frac{a}{s}}$
44.  $\oint (k-n)$   $\frac{1}{s^{n+1}}$
45.  $a^k \binom{n}{k}$   $\frac{1}{s} \left(1 + \frac{a}{s}\right)^n$
46.  $\frac{a^k}{k+1}$   $-\frac{1}{s} \log\left(1 - \frac{a}{s}\right)$
47.  $\frac{a^k}{k+2}$   $-\frac{s}{a^2} \log\left(1 - \frac{a}{s}\right) - \frac{1}{a}$
48.  $\frac{a^k}{k+3}$   $-\frac{s^2}{a^3} \log\left(1 - \frac{a}{s}\right) - \frac{2s+a}{2a^2}$
49.  $\frac{a^k}{(k+1)(k+2)}$   $\frac{s-a}{a^2} \log\left(1 - \frac{a}{s}\right) + \frac{1}{a}$
50.  $\frac{a^k}{(k+1)(k+3)}$   $\frac{s^2-a^2}{2a^3} \log\left(1 - \frac{a}{s}\right) + \frac{2s+a}{4a^2}$
51.  $\frac{a^k}{(k+2)(k+3)}$   $\frac{s^2-as}{a^3} \log\left(1 - \frac{a}{s}\right) + \frac{2s-a}{2a^2}$

52.  $\frac{a^k}{(k+1)(k+2)(k+3)} - \frac{(s-a)^2}{2a^3} \log(1-\frac{a}{s}) + \frac{3a-2s}{4a^2}$
53.  $\frac{a^{k+1} - b^{k+1}}{k+1} \log \frac{s-b}{s-a}$
54.  $\frac{k a^k}{k+1} \frac{1}{s-a} + \frac{1}{a} \log(1-\frac{a}{s})$
55.  $\frac{k a^k}{k+2} \frac{1}{s-a} + \frac{2}{a} + \frac{2s}{a^2} \log(1-\frac{a}{s})$
56.  $\frac{k a^k}{(k+1)(k+2)} \frac{a-2s}{a^2} \log(1-\frac{a}{s}) - \frac{2}{a}$
57.  $\frac{(-a)^k}{2k+1} \frac{1}{\sqrt{as}} \arctan \sqrt{\frac{a}{s}}$
58.  $\frac{(-a)^k}{(2k+1)(k+1)} \frac{2}{\sqrt{as}} \arctan \sqrt{\frac{a}{s}} - \frac{1}{a} \log(1+\frac{a}{s})$
59.  $\frac{L_k(x)}{k!} \frac{1}{s-1} e^{-\frac{x}{s-1}}$
60.  $\frac{H_k(x)}{k!} \frac{1}{s} e^{-\frac{2x}{s} - \frac{1}{s^2}}$
61.  $P_k(x) \frac{1}{\sqrt{s^2 - 2sx + 1}}$
62.  $J_k(x) \frac{1}{s} e^{-\frac{x}{2}} (s - \frac{1}{s})$
63.  $T_k(x) \frac{s-x}{s^2 - 2sx + 1}$
64.  $\frac{L_k^m(x)}{k!} \frac{\cos \pi m}{(s-1)^{m+1}} e^{-\frac{x}{s-1}}$
65.  $P_k^m(x) \frac{(2m)!}{2^m m!} \frac{s^m (1-x)^{\frac{m}{2}}}{(s^2 - 2sx + 1)^{m+\frac{1}{2}}}$

$$66. \quad \frac{a^k \sin wk}{k+1} \quad \frac{\cos w}{a} \arctan \frac{a \sin w}{s-a \cos w} + \frac{\sin w}{2a} \log \frac{s^2 - 2as \cos w + a^2}{s^2}$$

$$67. \quad \frac{a^k \cos wk}{k+1} \quad \frac{\sin w}{a} \arctan \frac{a \sin w}{s-a \cos w} - \frac{\cos w}{2a} \log \frac{s^2 - 2as \cos w + a^2}{s^2}$$

$$68. \quad \frac{a^k \sin \frac{\pi}{2} k}{k+1} \quad \frac{1}{2a} \log(1 + \frac{a^2}{s^2})$$

$$69. \quad \frac{a^k \cos \frac{\pi}{2} k}{k+1} \quad \frac{1}{a} \arctan \frac{a}{s}$$

$$70. \quad \frac{a^k \sin \frac{\pi}{2} k \cos w(k+1)}{k+1} \quad \frac{1}{4a} \log \frac{s^4 + 2a^2 s^2 \cos 2w + a^4}{s^4}$$

$$71. \quad \frac{a^k \cos \frac{\pi}{2} k \sin w(k+1)}{k+1} \quad \frac{1}{4a} \log \frac{s^2 + 2as \sin w + a^2}{s^2 - 2as \sin w + a^2}$$

$$72. \quad \frac{a^k \cos \frac{\pi}{2} k \cos w(k+1)}{k+1} \quad \frac{1}{2a} \arctan \frac{2as \cos w}{s^2 - a^2}$$

$$73. \quad \frac{a^k \sin \frac{\pi}{2} k \sin w(k+1)}{k+1} \quad \frac{1}{2a} \arctan \frac{a^2 \sin 2w}{s^2 + a^2 \cos 2w}$$

$$74. \quad \left(-\frac{1}{2}\right)_k (-a)^k \quad \frac{1}{\sqrt{s(s-a)}}$$

$$75. \quad \left(-\frac{1}{2}\right)_{\frac{k}{2}} a^k \cos \frac{\pi}{2} k \quad \frac{1}{\sqrt{s^2 - a^2}}$$

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# GROWTH OF YELLOW PIKEPERCH, *STIZOSTEDION VITREUM VITREUM* (MITCHILL), IN SOME IOWA LAKES, WITH A SUMMARY OF GROWTH RATES REPORTED IN OTHER AREAS<sup>1</sup>

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In connection with various projects of the Iowa Cooperative Fishery Research Unit, scales have been collected from a large variety of fishes for future study to determine the ages and growth rates of these fishes. The present report summarizes the data on the growth rate of yellow pikeperch collected from six lakes in the Iowa "lakes district" from 1941 to 1944.

The yellow pikeperch, *Stizostedion vitreum vitreum* (Mitchill), usually called the "walleye" by local fishermen, is one of the most important game fishes in Iowa's natural lakes. For many years the Iowa State Conservation Commission has planted thousands of fry and fingerlings to help maintain the pikeperch fishing. Numerous lake improvements and limitations on the catch have also been used in the management of this fishery resource in Iowa.

A study of the life history and growth rate of fishes is one of the most useful techniques in fishery research and management. An analysis of growth rates indicates where conditions are favorable for the fish, shows where fish populations are overcrowded and not in need of further planting, evaluates the success of earlier stocking, and serves as a scientific basis for regulation of the catch. The present paper, based as it is on a relatively small number of fish from several lakes, is presented primarily to give a general picture of the growth of yellow pikeperch in Iowa lakes for comparison with more detailed studies, which will appear later.

## METHOD OF STUDY OF GROWTH RATES

The ages and growth rates of most fishes may be determined from a study of the rings on their scales. The general methods used in these studies have been well described by Van Oosten (1929). In the present

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study and in most earlier studies, the growth rates have been calculated on the assumption that the scale radius and the length of the fish are directly proportional throughout life, since the number of scales remain constant. In Lake of the Woods, Minnesota, it was found that the body-scale relationship of the yellow pikeperch could best be described by an S-shaped curve and that growth rates calculated on a direct proportion basis were not entirely accurate (Carlander, 1945). Sufficient data were not available to determine the true body-scale relationship of the yellow pikeperch from these Iowa lakes and therefore the direct proportion method was used to give approximate growth rates. These growth data are sufficiently accurate for comparisons and the additional work required to determine the true body-scale relationship is probably justified only in detailed studies on individual populations. It was found that the body-scale relationship determined for the Lake of the Woods pikeperch would not give accurate growth calculations if used with pikeperch from other waters because the body-scale relationships differ in different populations (Carlander, Ms.).

The growth data in the present study were calculated using standard length in millimeters (the length from the tip of the snout to the end of the hypural plate), but are recorded in this paper as total lengths in inches (the length from the tip of the snout to the end of the tail with the two lobes of the tail together). Both standard and total lengths were measured on 83 of the fish and it was found that total length equals 1.198 standard lengths on pikeperch up to 450 millimeters standard length. On larger pikeperch, total length equaled 1.187 standard lengths. These factors were therefore used in converting standard to total lengths.

The yellow pikeperch were collected from the following Iowa lakes at the times and by the methods indicated below:

<i>Location</i>	<i>Time</i>	<i>Method</i>
EMMET COUNTY Mud Lake	April, 1944	Seine
DICKINSON COUNTY East Okoboji	October, 1941	Seine
West Okoboji	Aug.-Oct. 1941	Seine and angling
Spirit Lake	July, 1940	Angling
	Sept.-Dec. 1941	Seine, gillnet, angling
	June, 1943	Angling
	April-June, 1944	Gillnet and angling
Welch Lake	Sept.-Oct. 1941	Seine
Diamond Lake	Aug.-Sept. 1941	Seine

A total of 216 yellow pikeperch were examined from these lakes.

#### SIZES OF YELLOW PIKEPERCH IN VARIOUS AGE CLASSES

The smallest yellow pikeperch examined in this study was 6.9 inches in total length and was less than one year old; the largest was 26.7 inches long and was twelve years old. Roman numerals are usually used to indicate the age class to which a fish belongs. For example, a fish collected

**TABLE 1**  
**THE TOTAL LENGTHS OF YELLOW PIKEPERCH FROM VARIOUS IOWA LAKES BY AGE**  
**CLASSES AT TIME OF CAPTURE**

Age Class	Lake	Date	Number of fish	Total length in inches	
				Mean	Range
O .....	Diamond	Aug.-Sept., 1941	2	7.0	6.9-7.2
I .....	Mud	April, 1944	7	7.8	7.2-8.3
	Diamond	Aug.-Sept., 1941	37	7.9	6.9-9.6
	West Okoboji	Aug.-Oct., 1941	4	8.9	7.8-10.5
	Spirit	October, 1942	1	10.7	.....
	<i>Totals</i>		49	8.0	6.9-10.7
II .....	Mud	April, 1944	2	9.7	9.5-9.8
	Spirit	July, 1940	2	9.4	8.6-10.2
		Sept.-Dec., 1941	5	10.8	9.7-11.7
		October, 1942	4	11.8	11.3-13.1
	Diamond	Aug.-Sept., 1941	18	12.2	10.5-14.4
	West Okoboji	Aug.-Oct., 1941	36	11.0	9.2-12.5
	Welch	October, 1941	1	14.2	.....
	<i>Totals</i>		68	11.3	8.6-14.4
III .....	Spirit	March, 1943	5	14.3	13.7-14.8
		April-June, 1944	3	15.2	13.9-16.0
		June, 1943	1	13.0	.....
		October, 1942	9	14.1	13.0-14.7
		Sept.-Dec., 1941	5	16.5	14.9-18.5
	West Okoboji	Aug.-Oct., 1941	8	13.4	10.0-15.7
	Welch	September, 1941	1	14.4	.....
	<i>Totals</i>		32	14.4	10.0-18.5
IV .....	Spirit	March, 1943	1	16.0	.....
		April-June, 1944	5	16.8	15.8-17.8
		Sept.-Dec., 1941	5	17.3	16.8-17.8
		October, 1942	3	17.3	16.3-18.2
		Sept.-Oct., 1941	5	17.7	16.5-18.7
	<i>Totals</i>		19	17.2	15.8-18.7
V .....	Spirit	April, 1944	1	18.1	.....
		October, 1942	6	18.9	17.2-20.9
		November, 1941	1	20.0	.....
	East Okoboji	Sept.-Oct., 1941	7	19.0	17.7-20.7
	<i>Totals</i>		15	19.0	17.2-20.9
VI .....	Spirit	March, 1943	1	19.3	.....
		April-June, 1944	4	19.0	18.7-19.1
		October, 1942	2	20.7	20.1-21.1
		November, 1941	1	19.0	.....
		November, 1945	2	19.4	18.2-20.5
	West Okoboji	September, 1941	1	19.7	.....
	East Okoboji	Sept.-Oct., 1941	5	20.3	18.4-21.7
	<i>Totals</i>		16	19.7	18.2-21.7
VII .....	Spirit	March, 1943	1	19.8	.....
		April, 1944	1	20.0	.....
		October, 1942	6	21.0	19.2-22.8
		November, 1945	2	19.3	18.4-20.1
	<i>Totals</i>		10	20.4	19.2-22.8
VIII .....	West Okoboji	June, 1942	1	20.5	.....
	East Okoboji	October, 1945	1	24.8	.....
	Spirit	October, 1942	1	22.4	.....
	<i>Totals</i>		3	22.6	20.5-24.8
IX .....	Spirit	October, 1942	1	23.8	.....
XII .....	Spirit	March, 1943	1	26.7	.....

in the same year in which it was hatched belongs to the O Age Class, and three years later the same fish would have three annuli and would belong to the III Age Class. The oldest yellow pikeperch ever reported belonged to the XVIII Age Class (Juday and Schloemer, 1938), but very few pikeperch reach ten years of age.

The growth rates of fishes are much more elastic than are those of most warmblooded animals and are readily modified by various environmental conditions. It is because of this adaptation to the environment that the study of fish growth rates is particularly valuable as an indicator

TABLE 2

A COMPARISON OF THE AVERAGE TOTAL LENGTHS OF YELLOW PIKEPERCH IN AGE CLASSES III, V, AND VII FROM VARIOUS WATERS

Locality AGE CLASS III	Authority	Number of fish	Average total length in inches
Lake Nipigon, Ontario	Hart, 1928*	2	9.5
Lake Erie	Adamstone, 1922*	...	12.2
Prairie Provinces, Canada	Bajkov, 1930*	...	13.2
Lake Erie	Deason, 1933*	60	13.5
Ohio lakes	Langlois	167	13.5
Lake of the Woods	Carlander, Ms.*	152	13.6
Quetico, Ontario	Lindeborg, 1941	6	13.9
Minnesota lakes	Eddy and Carlander, 1942*	1,189	14.2
Iowa lakes	Present study	32	14.1
Wisconsin lakes	Juday and Schloemer, 1938	66	15.0
Trout Lake, Wisconsin	Schloemer and Lorch, 1941†	45	15.5
Ontario watershed, N. Y.	Greeley, 1940	14	17.0
Nortis Reservoir, Tenn.	Eschmeyer and Jones, 1941	64	20.5
AGE CLASS V			
Lake Abitibi, Ontario	Hart, 1928*	1	11.9
Lake Nipigon, Ontario	Hart, 1928*	9	11.2
Prairie Provinces, Canada	Bajkov, 1930*	...	16.3
Quetico, Ontario	Lindeborg, 1941	6	16.5
Lake of the Woods, Minn.	Carlander, Ms.*	1,580	16.8
Minnesota lakes	Eddy and Carlander, 1942*	642	18.1
Wisconsin lakes	Juday and Schloemer, 1938	139	18.1
Lake Erie	Deason, 1933*	4	18.8
Iowa lakes	Present study	15	19.0
Ontario watershed, N. Y.	Greeley, 1940	6	19.7
Ohio lakes	Langlois	23	19.9
Trout Lake, Wisconsin	Schloemer and Lorch, 1941†	71	20.3
AGE CLASS VII			
Lake Abitibi, Ontario	Hart, 1928*	4	13.8
Lake Nipigon, Ontario	Hart, 1928*	2	15.2
Prairie Provinces, Canada	Bajkov, 1930*	...	18.8
Lake of the Woods, Minn.	Carlander, Ms.*	101	19.2
Quetico, Ontario	Lindeborg, 1941	17	20.2
Iowa lakes	Present study	10	20.4
Wisconsin lakes	Juday and Schloemer, 1938	117	21.2
Minnesota lakes	Eddy and Carlander, 1942*	58	23.1
Trout Lake, Wisconsin	Schloemer and Lorch, 1941†	60	23.6
Ohio lakes	Langlois	3	24.6

\* Standard lengths converted to total lengths using the coefficients given by Carlander and Smith (1945).

† Standard lengths converted to total lengths using the coefficient given by Schloemer and Lorch (1941).

of conditions in various waters. The variation of growth in the yellow pikeperch is shown in Table 1 where the sizes of the fish in various age classes are compared. Some of the III Age Class pikeperch are smaller than the largest I Age Class fish. Speaker (1936) reports yellow pikeperch up to 13.5 inches long while less than one year old in an Iowa rearing pond. Some of the three-year-old fish in the present study were not this large. It is obvious that one cannot tell the age of a fish accurately by simply comparing its size with that of other fishes of known age.

Direct comparison of the average sizes of fish in the same age classes gives only an approximation of the differences between growth rates in various waters because the fish have been collected at different times during the year. The fish in Age Class I from Mud Lake have not yet started their second summer's growth while those from Spirit Lake have completed the second summer's growth. In the older age classes, however, such a comparison may have some value since the annual growth in the later years is comparatively less than in the early years of life. For comparative purposes the average lengths of yellow pikeperch in the Age Classes III, V, and VII in the Iowa lakes and in other waters throughout the country are given in Table 2. The rate of growth in the Iowa lakes seems to be about average or a little faster than average for the series of waters for which growth studies have been reported.

The calculated growth rates, using the scale measurements in the calculation of growth during the earlier years of life, give a more convenient and probably a more accurate method of comparing the growth in different waters (Table 3). On the basis of these data, the growth of yellow pikeperch in West Okoboji is a bit slower than that in Spirit Lake, which in turn is slower than that in East Okoboji. The growth in the other lakes appears to be even more rapid, but the fish are too young for valid comparison.

The increase in length is greatest the first year, and each successive year the annual increase is less. The average annual increment, as given in Table 3, was calculated using only those fish which completed the growth for the year of life in question and therefore is not always exactly equal to the difference in lengths at the beginning and the end of the year given for the combined group of fish in the line above. For example, the average calculated total length for the fish at the end of the third year included data from a large number of pikeperch which did not reach the end of the fourth year.

A comparison of the average calculated growth for the Iowa pikeperch with that reported from other waters indicates that the Iowa pikeperch show about an average rate of growth (Table 4).

#### FACTORS AFFECTING THE GROWTH RATES OF YELLOW PIKEPERCH

The available data are not complete enough to determine the factors which are responsible for the differences in the growth rates of the yellow pikeperch in these Iowa lakes. It may be of some significance, however, that of the three lakes from which samples of older fish were

TABLE 3  
THE CALCULATED GROWTH OF YELLOW PIKEPERCH IN VARIOUS IOWA LAKES

Lake	No. of fish	Average calculated total length in inches at each annulus											
		1	2	3	4	5	6	7	8	9	10	11	12
West Okoboji	50	5.0	9.2	11.7	15.9	15.9	17.6	18.0	19.7	...	...	...	...
Spirit	80	4.9	8.8	12.4	14.8	16.9	18.5	19.8	21.5	23.2	24.7	25.9	26.6
East Okoboji	18	5.2	9.5	12.9	15.7	17.7	19.4	21.9	23.8	...	...	...	...
Welch	2	5.4	10.2	12.5	...	...	...	...	...	...	...	...	...
Diamond	57	5.2	10.0	...	...	...	...	...	...	...	...	...	...
Mud	9	6.8	...	...	...	...	...	...	...	...	...	...	...
Combined	216	5.0	9.2	12.4	15.0	17.1	18.6	19.9	21.5	23.2	24.7	25.9	26.6
Annual increment	...	5.0	4.2	3.1	2.8	2.3	1.8	1.4	1.7	1.7	1.3	1.2	0.7

secured, the growth was slowest in the deepest lake, West Okoboji, and most rapid in the shallowest lake, East Okoboji. Shallow lakes are usually more productive than deep lakes.

The rapid growth in Mud, Diamond, and Welch lakes was probably associated with low population densities. These lakes are subject to frequent winter kill and have been used upon occasion as rearing areas for yellow pikeperch with the fish seined out at the end of the growing season. Population density seems to be an important factor in modifying the growth rates of yellow pikeperch (Eddy and Carlander, 1940). The rapid growth of yellow pikeperch in Norris Reservoir, Tennessee, was probably partly the result of the recent introduction and fairly low population density of the fish (Eschmeyer and Jones, 1941).

There is also a tendency for the growth of the pikeperch to be slower in the northernmost lakes (Tables 2 and 4). Bennett (1937) pointed out that the growth of the largemouth bass is more rapid toward the south. Similar trends have been shown for the long-eared and green sunfishes in Michigan (Hubbs and Cooper, 1934) and for a number of species in Minnesota (Eddy and Carlander, 1940). The increase in growth rate toward the south may be the result of longer growing seasons and of higher summer temperatures, which increase the metabolic processes of the fish. The growth of yellow pikeperch in Lake of the Woods was found to be more rapid during summers with high July and August mean temperatures (Carlander, 1945).

#### COEFFICIENT OF CONDITION

The rate of growth is one of the most important indicators of the health and success of fish in a given body of water. Another indicator of some value is the coefficient of condition,  $K$ , which has been discussed by Hile (1936):

$$K = \frac{W 10^5}{L^3}$$

if  $W$  = weight in grams  
and  $L$  = standard length in millimeters

This coefficient gives a convenient measure of the plumpness of the fish. Heavy-bodied fish have higher  $K$  values than do thin, starved fish. In some species, the value of  $K$  varies with the length of the fish or with the time of the year in which the fish is caught. A comparison of the  $K$  values of these Iowa yellow pikeperch did not show a consistent tendency to increase or decrease with increase in the length. Neither were any seasonal trends detected. In Trout Lake, Wisconsin, (Schloemer and Lorch, 1942), and in Lake of the Woods, Minnesota (Carlander, 1945), there was a tendency for the value of  $K$  to be higher in yellow pikeperch 3 to 6 years old than in younger or older fish. A similar tendency may have been present in the Iowa data but it was not pronounced enough to alter comparisons. The data from each lake were therefore combined, without regard to length or to season, for comparison of the condition

TABLE 4  
CALCULATED GROWTH OF YELLOW PINEPERCH REPORTED FROM VARIOUS WATERS

Locality	Number of fish	Average calculated total length in inches at each annulus									
		1	2	3	4	5	6	7	8	9	10
Clear Lake, Wisconsin* (Schloemer and Lorch, 1942)	77	4.0	8.0	10.7	12.6	14.0	15.7	..	...	..	...
Lake of the Woods, Minn.† (Carlander, 1945)	2 898	6.5	9.2	11.5	13.5	14.8	16.6	18.1	19.8	21.5	22.6
Lake Erie‡ (Adamstone, 1922)	25	4.7	8.2	11.1	13.6	15.6	17.5	19.4	21.1	22.5	24.0
Lake Erie (Deason, 1933)	1,430	4.2	8.4	11.3	14.8	18.0	20.8	...	...	...	...
Iowa lakes	216	5.0	9.2	12.4	15.0	17.1	18.6	19.9	21.5	23.2	24.7
Wisconsin lakes§ (Schloemer and Lorch, 1942)	1,132	5.4	9.8	13.2	15.9	17.8	19.5	21.8	23.3	24.8	26.1
Trout Lake, Wisconsin (Schloemer and Lorch, 1942)	429	5.3	9.7	13.7	16.6	19.0	20.7	21.7	22.3	23.1	23.3
Minnesota lakes   (Eddy and Carlander, 1939)	6,599	4.9	9.1	12.7	15.8	19.1	21.6	24.2	26.6	28.2	...
Bear Lake, Wisconsin* (Schloemer and Lorch, 1942)	5	6.5	11.9	17.2	20.3	22.6	25.3	23.9	25.3	26.8	..
Norris Reservoir, Tenn. (Eschmeyer and Jones, 1941)	96	8.3	16.0	20.5	22.4	...	...	...	...	...	...

\* Standard lengths converted to total lengths using the coefficient given by Schloemer and Lorch, 1941. Clear Lake was the lake showing slowest growth of 39 Wisconsin lakes studied, and Bear Lake showed the fastest growth.

† Standard lengths converted to total lengths using the coefficients given by Carlander and Smith, 1945. Growth calculated using corrected body-scale relationship.

‡ Standard lengths converted to total lengths using the coefficients given by Carlander and Smith, 1945.

§ An unweighted average of 39 lakes.

|| Fork lengths converted to total lengths using the coefficients given by Carlander and Smith, 1945.

in various lakes (Table 5). In general, the yellow pikeperch in these Iowa lakes seem to be in good condition, with relatively high *K* values. The lakes in which the pikeperch show rapid growth are not necessarily the ones in which the fish are the fattest and have high *K* values.

TABLE 5  
AVERAGE COEFFICIENT OF CONDITION, *K*, OF YELLOW PIKEPERCH FROM VARIOUS LAKES

Lake	Number of fish	Standard Length in mm.	Mean, <i>K</i> Value
Mud . . . . .	9	152-208	1.26
West Okoboji . . . . .	50	165-435	1.37
Welch . . . . .	2	302-306	1.52
East Okoboji . . . . .	17	351-530	1.66
Spirit . . . . .	67	207-570	1.71
Diamond . . . . .	57	146-305	1.81
Iowa lakes, combined . . . . .	202	146-570	1.64
Trout Lake, Wisconsin (Schloemer and Lorch, 1912)	266	130-640	1.45
Lake of the Woods, Minnesota (Carlander, 1945)	368	150-550	1.47

#### SUMMARY

1. The growth rates of 216 yellow pikeperch from six Iowa lakes were determined from examination of their scales and were calculated by the direct proportion method.

2. The pikeperch ranged from less than one year to over twelve years in age and a considerable variation in the growth rates was observed.

3. Growth in the Iowa lakes is about or a little above average when compared with growth rates reported from other waters throughout the country.

4. Richness of the lake, population densities, and length of growing seasons are suggested as factors modifying the growth in different waters.

5. The average *K* of 202 yellow pikeperch from Iowa lakes was 1.64, which is somewhat higher than that reported from other waters.

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# REINFECTION WITH *TRYPANOSOMA LEWISI* AND RECURRENCE OF REPRODUCTION IN RECOVERED AND NEAR-RECOVERED RATS<sup>1</sup>

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It has been reported by Becker and Gallagher that the host reaction which clears the blood of reproducing *Trypanosoma lewisi* is inhibited by sodium salicylate treatment of the rat host (1). Reappearance of the reproducing population, however, did not follow the treatment of rats still harboring adult trypanosomes or recovered rats reinjected with adult trypanosomes. The present authors have experimented further and without success in similar efforts with near-immune (i.e., still harboring adult trypanosomes) and immune rats. Likewise, inoculations of salicylate-treated recovered rats with large numbers of trypanosomes in the reproductive phase have so far resulted only in the rather prompt destruction of the microorganism in the immune host, whether introduced intraperitoneally or intravenously. However, when both donor and receptor rats were treated, reinfection with reproduction followed in certain, but by no means all, cases. As will be brought out subsequently, it appears that trypanocidal rather than anti-reproductive reaction products are responsible for the refractory animals.

## MATERIALS AND METHODS

Strain of rats and of trypanosomes, method of drug administration, enumeration of trypanosomes, and staining were described in the previous paper (1). In the present work the criterion of reproduction and tempo of reproduction was standard deviation instead of the percentage of "division forms," as formerly. Degrees of freedom were not used in the calculation. Taliaferro and Taliaferro (2) employed the coefficient of variation for the same purpose, but this constant has the objectionable feature that it measures variability relative to the mean, while all that is required is measuring variability. Coefficients of variation were calculated, however, and appear in the tables, but not in the graphs. Fifty specimens were usually measured from each slide stained in Wright's, though in some cases the number was 60, 75, or 100. In case the specimens were extremely rare, only 25 or 40 trypanosomes were measured. Notations were made on the presence or absence of actually dividing specimens in the smear. A number of records were made of the percent-

<sup>1</sup>Supported in part by grant to Project 40, Industrial Science Research Institute, Iowa State College.

age of dividing specimens, but the values were so variable that it is believed they are of little significance, and are not here reported.

Discussions of the nature of immunity to *T. lewisi* and of the physiological effects of sodium salicylate appear in the previous paper (1).

### EXPERIMENTAL DATA

Notes from the protocol are presented as a background for understanding of the circumstances under which reinfections were obtained.

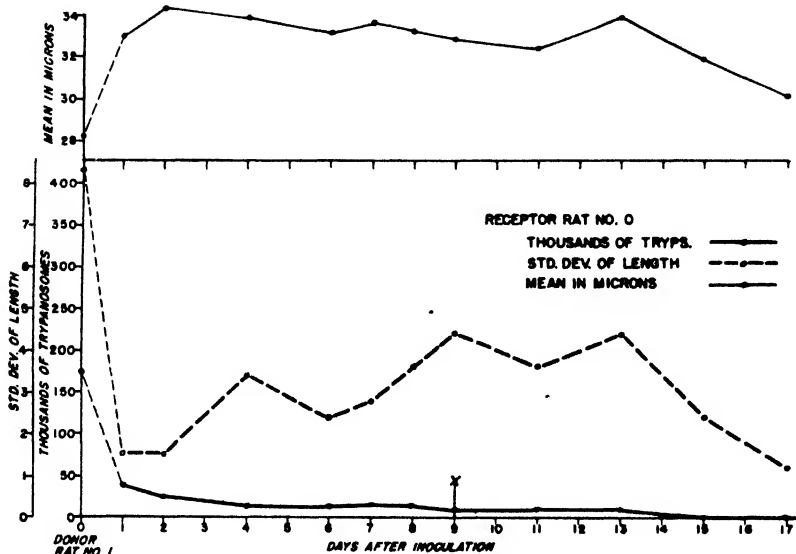


FIG. 1. Course of infection in receptor rat No. 0. Standard deviation of length is expressed in microns, and "thousands of trypanosomes" is the count per mm.<sup>3</sup> of blood. Points on O-ordinate connected by broken lines with analogous points on ordinate for day 1 represent the pertinent data describing the condition of the trypanosomes in the donor rat at the time the receptor rat was injected. Vertical line perpendicular to the abscissa and capped by x marks last day salicylate was administered.

### SERIES I

June 12. Seven 154 g. female rats of same litter were inoculated i.p. with 400,000 *T. lewisi*.

June 19. Trypanosomes have attained adult stage in the seven rats. Administered each rat sodium salicylate in 6.0 per cent aqueous solution with the dosage at 540 mg./kg.

June 20, 22, 23, 24, 26. Dosings repeated.

June 24. Adult trypanosomes persisting in 2 rats (Nos. 0 and 1); five rats trypanosome-free. Each rat injected i.v. and i.p., half and half, with 2 cc. of diluted blood containing  $18 \times 10^7$  trypanosomes in fourth day of infections in untreated rats.

June 25. Rats Nos. 2-6 trypanosome-free; rats Nos. 0 and 1 with adult stages.

June 28. Rats Nos. 2-6 trypanosome-free; rat No. 0 with 18,000 adult trypanosomes/mm.<sup>3</sup> of blood; rat No. 1 with 31,000/mm.<sup>3</sup>

Administered each rat by lavage 135 mg. sodium salicylate in 9.0 per cent aqueous solution.

Injected each rat i.p. with  $175 \times 10^6$  four-day trypanosomes in multiplicative phase

from donor rats that had been treated with 90 mg. doses of sodium salicylate at time of inoculation and at end of first, second, and third days.

June 29. Blood of rats Nos. 0, 1, and 2 positive for *T. lewisi*; four other rats negative this day and thereafter.

Subsequent doses of sodium salicylate were administered to the three positive rats as follows, according to days of the infections: 1-4, 90 mg.; 5, 135 mg.; 6-9, 90 mg.; 10-17, 0 mg.

Tables 1 and 2 record the pertinent data regarding the infections in rats Nos. 0, 1, and 2. The courses of infection in the three rats presented striking contrasts. That for rat No. 0 is charted in Figure 1.

Rat No. 0 had 18,000 adult trypanosomes/mm.<sup>3</sup> of blood immediately prior to inoculation with 1 cc. of blood from donor rat No. 1. The latter rat, in the fourth day of the infection, had  $175 \times 10^3$  trypanosomes/mm.<sup>3</sup> of blood, and 100 measured trypanosomes had mean length of 28.2  $\mu$  and standard deviation of 8.3  $\mu$  (Table 1). The former value is comparatively low and the latter comparatively high, and both are indicative of a rapidly multiplying population (cf. Taliaferro and Palinova (3)).

Forms in the process of division could readily be found in stained smears. At the end of a day the parasite count had more than doubled in the receptor rat, no examples of division were to be found in the smears, the mean was 33.0  $\mu$ , and the standard deviation 1.5  $\mu$ . On the second day the situation was but little different, except that the count was lower and dividing forms were beginning to appear in the blood. Thereafter the count showed a tendency to drop until the blood was cleared by the nineteenth day, this despite observed reproduction and moderately high standard deviations on fourth to fifteenth days. Observation of dividing forms on the eleventh day and moderately high standard deviations to the fifteenth day prove that reproduction continued for several days after the last dose of salicylate on the ninth day. It is to be noted that the means continued high throughout even while reproduction was proceeding, indicating, to our mind, selection of the small types (Plate A: 5 and 6) for destruction.

Rats Nos. 1 and 2 were also inoculated with  $175 \times 10^6$  four-day trypanosomes from donor rat No. 1. The first rat had in its blood just prior to inoculation 31,000 trypanosomes/mm.<sup>3</sup> and, as is the case of rat No. 0, they were adults in the sixteenth day of the infection. Despite the introduction of so many trypanosomes by inoculation, the parasite count decreased steadfastly from 0 day to the eighth and eleventh days (Table 2). At no time could dividing forms be found in the smears, but standard deviations of 2.0-2.4  $\mu$  from fourth to eleventh days and coefficient of variations of 6.4-7.7 per cent during the same period suggest that some reproduction was occurring. The rat was found dead from unknown causes on the twelfth day.

Rat No. 2 was inoculated under the same circumstances as the preceding except that it had completely recovered. The parasitemia (V. Table 2) did not exceed 500 trypanosomes/mm.<sup>3</sup> after the morning following the inoculation, and by the twelfth day the blood was trypanosome-free microscopically, but actually dividing forms were to be found in

TABLE 1

## DATA PERTAINING TO COURSE OF INFECTION IN RECEPTOR RAT NO. 0

(Trypanosomes/1,000 = thousands/mm.<sup>3</sup> of blood; Std. Dev. = standard deviation for lengths in microns; C. V. % = coefficient of variation for lengths in per cent. Mean in  $\mu$  = mean lengths in microns; \*after day designation = dividing forms noted; x after day designation = last day of infection on which salicylate was administered.)

Kind of Data	Donor Rat No. 1 4th day*	Receptor Rat No. 0—Days after inoculation											
		1	2*	4*	6*	7*	8*	9x*	11*	13	15	17	19
Trypano- somes/1,000.	175	38	25	15	15	17	13	9	10	9	<1	<1	0
Std. Dev.....	8.3	1.5	1.5	3.4	2.4	2.8	3.6	4.4	3.6	4.4	2.4	1.2	..
C. V. %.....	29.4	4.5	4.4	10.0	7.2	8.3	10.9	13.6	11.1	13.0	7.5	4.0	..
Mean in $\mu$ ..	28.2	33	34.3	33.9	33.2	33.7	33.2	32.9	32.4	33.9	31.9	30.1	..

TABLE 2  
RECEPTOR RATS NO. 1 AND NO. 2  
(Data as for Table 1)

Kind of Data	Receptor Rat No. 1 Days after inoculation							Receptor Rat No. 2 Days after inoculation						
	0	1	2	4	6	8	11†	1*	2*	4*	6*	8	9x	11
Trypano- somes/1,000.....	31	19	11	12	7	5	5	0.5	0.5	0.4	0.4	0.3	0.3	<0.1
Std. Dev.....	1.9	.	0.7	2.4	2.1	2.4	2.0	3.6	3.1	1.7	2.1	2.0	..	..
C. V. %.....	5.7	..	2.2	7.7	6.8	7.6	6.4	12.7	10.8	5.6	6.5	6.7	..	..
Mean in $\mu$ .....	33.2	..	32.5	31.3	31.1	31.7	31.0	28.4	28.7	30.2	32.5	30.0	..	..

† Salicylate last administered on ninth day.

the blood continuously until the eighth day. The standard deviations fluctuated between  $1.7\ \mu$  and  $3.6\ \mu$ , the means between  $28.4\ \mu$  and  $32.5\ \mu$ . The actually dividing forms observed in this rat were not the large and small types characteristic of normal reproduction (Plate A: 1, 3, and 6), but of the type which Taliaferro and Palinova (3) observed in *T. duttoni* and *T. lewisi* infections and considered to be double monsters in which the component parts remained united instead of separating. The following

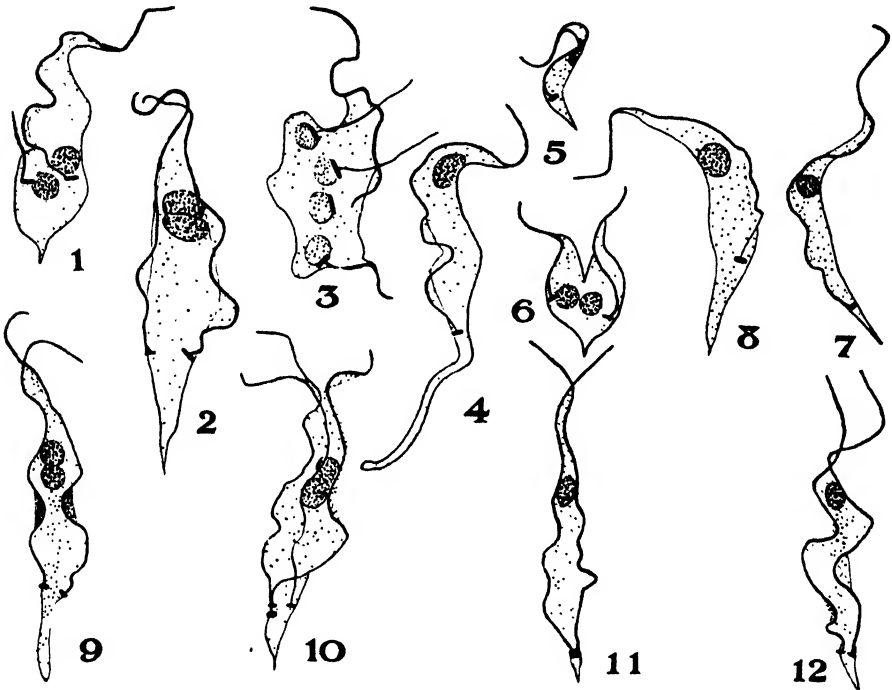


PLATE A. Developmental forms of *Trypanosoma lewisi* encountered during measuring: 7, normal adult; 4, intermediate between 7 and 8; 8, "transitional," the type which undergoes binary (1 and 2) or multiple (3) division to form the small types 5 and 6, which may in turn undergo division, as in 6; 9-12, stages in adult division seen only in receptor rat No. 2 except for a single specimen in receptor rat No. 4 on the last day of the multiplicative phase. X1,560.

combinations of organelles were noted: (a) 1 nucleus, 2 flagella, 1 parabasal body (Plate A: 11); (b) 1 nucleus, 2 flagella, 2 parabasal bodies (Plate A: 12); (c) 1 dividing nucleus, 2 flagella, 2 parabasal bodies; (d) 2 nuclei, 2 flagella, 2 parabasal bodies (Plate A: 9); (e) 1 dividing nucleus, 3 flagella, 3 parabasal bodies (Plate A: 10). All the preceding forms had intact cytoplasms, but one specimen was seen with the split between the two sets of organelles almost completed. We consider all these forms to represent adult fission, as contrasted with the familiar



TABLE 3  
RECEPTOR RAT NO. 3  
(Data as for Table 1)

Kind of Data	Donor Rat No. 2 4th day*	Receptor Rat No. 3—Days after inoculation																
		1*	2*	3*	4*	5*	7*	9*	10*	11*	12*	13*	14*	15*	16*	17*	19	21
Trypano- somes/1,000	350	2	5	18	75	220	155	582	.	490	738	600	280	115	50	38	<1	0
Std. Dev.....	5.1	3.2	5.6	6.1	6.6	5.9	5.5	5.3	...	5.9	5.8	3.4	6.3	6.2	6.1	7.3	3.7	..
C. V. %....	20.5	13.4	19.9	23.0	26.8	18.6	19.1	18.2	...	22.6	21.5	12.5	23.1	22.0	18.5	25.2	16.2	..
Mean in $\mu$ ....	24.9	23.4	28.1	26.5	24.7	31.7	28.1	29.1	.	26.1	27.0	27.2	27.2	28.2	32.8	29.0	22.8	..

appearances in the multiplicative phase of the normal cycle (Plate A: 1, 3, 4, 5, 6, 8).

Binary fission similar to that of adults is occasionally encountered among the large "intermediate" types (Plate A: 2).

#### SERIES II

July 5. Three male and three female rats of young litter with mean weight of 126 g. each injected i.p. with 500,000 adult *T. lewisi*.

July 9. Trypanosomes found in blood of all except No. 1.

July 12. Rats Nos. 1-6 are trypanosome-free.

July 13. Mean wt. of litter 151 g. To each rat is administered 1 cc. of 9.0 per cent sodium salicylate solution on this and five succeeding days.

July 14. Each of the six rats is injected i.p. with diluted blood containing  $1 \times 10^6$  *T. lewisi* in fourth day of infection in untreated rats.

July 15-19. Blood negative.

July 20. Rats Nos. 1, 2, 3, and 5 each injected i.p. with  $175 \times 10^6$  four-day *T. lewisi* in diluted blood from donor rat No. 2 which had received 90 mg. salicylate daily for four days previously. Salicylate dose raised to 120 mg. for all six receptor rats today and henceforth.

July 21. Blood of rats Nos. 1, 2, and 4 negative; No. 3 positive.

July 22. Injected rats No. 4 and 6 i.p. with  $300 \times 10^6$  four-day *T. lewisi* in diluted blood from donor rat No. 3 which had received 90 mg. salicylate daily for the four previous days.

July 23. Trypanosomes present in blood of rat No. 4; rat No. 6 negative today and thereafter.

The data for the infections in rats Nos. 3 and 4 are recorded in Tables 3 and 4, respectively, and the courses of the infections are charted in Figures 2 and 3, respectively.

When inoculated on July 20, rat No. 3 (♀) was a recovered, trypanosome-free animal. The injected trypanosomes were from donor rat No. 2 whose blood, as Table 3 shows, had a parasitemia of 350,000 trypano-

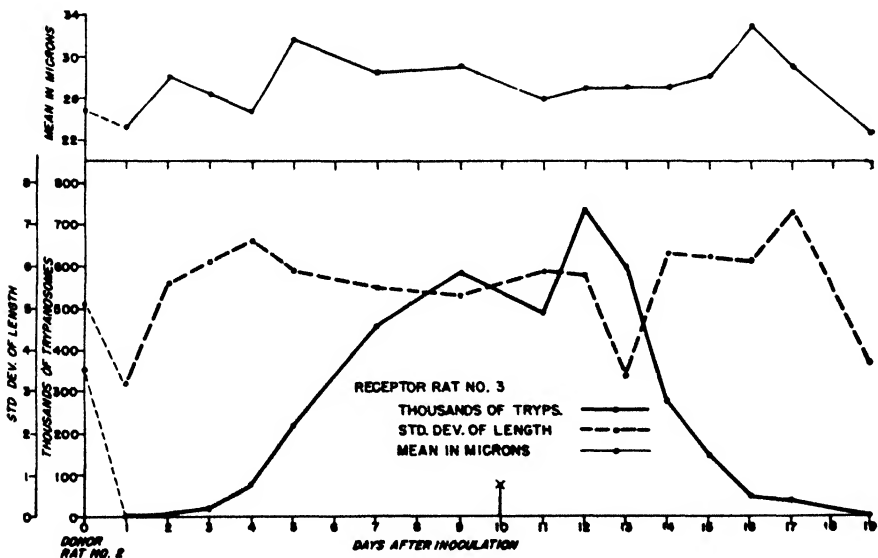


FIG. 2. Course of infection in receptor rat No. 3. (See explanatory notes under Fig. 1.) Note that the scale of the ordinate is reduced 50 per cent.

TABLE 4  
Receptor Rat No. 4  
(Data as for Table 1)

Kind of Data	Donor Rat No. 3 4th day*	Receptor Rat No. 4—Days after inoculation													
		1*	2*	3*	4*	5*	6*	7*	8*	9*	10*	11	12	13	15
Trypano- somes/1,000.....	300	3	24	53	111	175	225	240	300	328	65	35	12	3	3
Std. Dev.....	4.1	2.8	1.4	6.1	6.3	5.8	6.0	4.6	5.1	6.9	5.6	3.7	1.7	1.2	1.6
C. V. %.....	13.2	9.4	4.8	21.7	21.0	18.7	20.0	15.0	16.2	19.8	15.0	12.5	5.7	4.2	5.7
Mean in $\mu$ .....	31.0	30.0	29.1	28.1	29.6	31.0	30.0	30.7	31.6	34.9	37.3	29.7	29.8	28.9	28.2

somes/mm.<sup>3</sup> in a highly reproductive state, indicated by the standard deviation of 5.1  $\mu$  and mean length of 24.9  $\mu$ . The parasite count for the receptor rat showed an upward trend until the twelfth day, two days after the last dose of salicylate, then a moderately rapid drop until the last flagellates were seen on the nineteenth day. Dividing specimens were seen continuously through the seventeenth day. The standard deviations were high and the mean lengths low, with two notable exceptions, throughout.

Receptor rat No. 4 ( $\delta$ ) was likewise recovered and trypanosome-

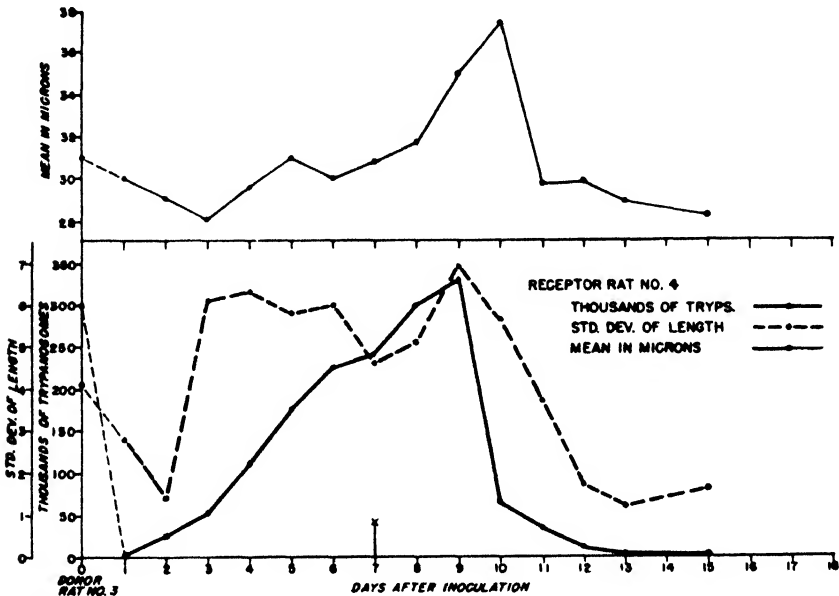


FIG. 3. Course of infection in receptor rat No. 4. (See explanatory notes under Fig. 1.)

free. The data for this animal and donor rat No. 3 appear in Table 4. It is obvious that the population from which the inoculum was obtained was in a highly reproductive state. The counts rose until the ninth day, two days after salicylate was discontinued, and then dropped precipitously. Dividing trypanosomes were seen through the tenth day. The standard deviations were high from the third to the eleventh day, when reproduction appears to have ceased.

### SERIES III

The receptor rats of this series were not litter mates, and fell into three groups under observation at different times. None of them received salicylate treatment, but all of them were inoculated i.p. with large numbers of trypanosomes from treated donor rats. Receptor rats Nos. 5 ( $\delta$ ), 6 ( $\delta$ ) and 7 ( $\varphi$ ) had no record of *T. lewisi* infection and weighed

TABLE 5  
Receptor Rat No. 5  
(Data as for Table 1)

Kind of Data	Donor Rat No. 4 4th day*	Receptor Rat No. 5—Days after inoculation							
		1*	2*	3*	4	5	7	10	18
Trypano- somes/1,000 . . . . .	380	50	140	355	465	377	260	80	13
Std. Dev. . . . .	7.0	8.9	5.7	5.1	4.1	2.3	2.1	1.5	1.0
C. V. % . . . . .	22.6	30.8	16.5	17.6	12.4	6.8	6.6	5.1	3.6
Mean in $\mu$ . . . . .	31.0	29.0	31.3	29.2	32.7	33.4	31.0	29.6	28.3

155–185 g. Receptor rats Nos. 8–15 were recovered and trypanosome-free, and of about the same weight. Rats Nos. 5–7 were inoculated i.p. with  $217 \times 10^6$ ,  $85 \times 10^6$  and  $100 \times 10^6$  trypanosomes in a high reproductive tempo, respectively, in diluted blood from donor rats which had received salicylate treatment since the inoculation date. It will be noted (Tables 5, 6, and 7) that dividing trypanosomes were observed only during the first three days of these infections, and that the numbers rose sharply to peaks on the fourth (rat No. 5) and third (rats Nos. 6 and 7) days, then dropped sharply. The standard deviations were high during the periods of reproductive activity, then dropped to lower levels (Fig. 4, 5, and 6).

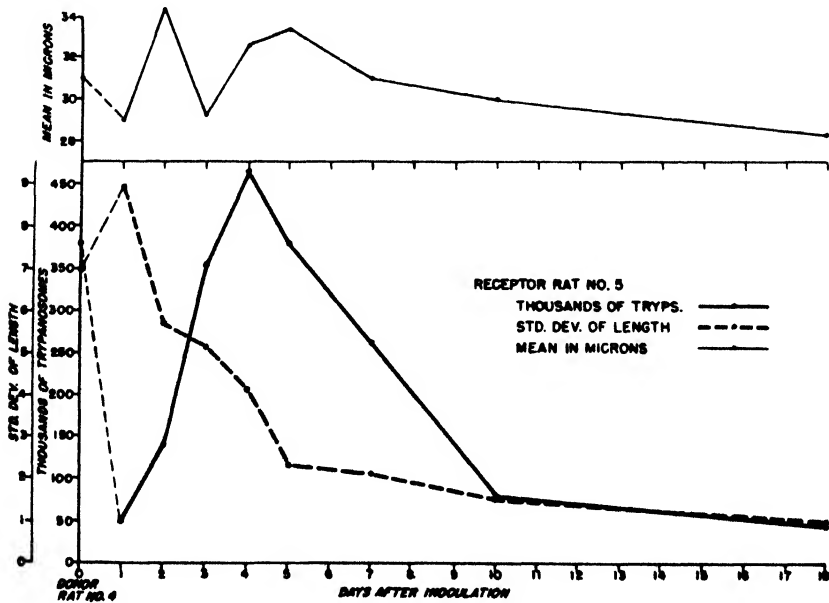


FIG. 4. Course of infection in receptor rat No. 5. (See explanatory notes under Fig. 1.)

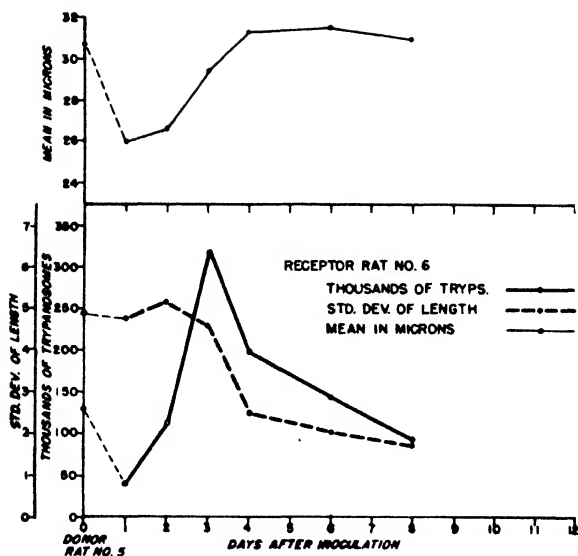


FIG. 5. Course of infection in receptor rat No. 6. (See explanatory notes under Fig. 1.)

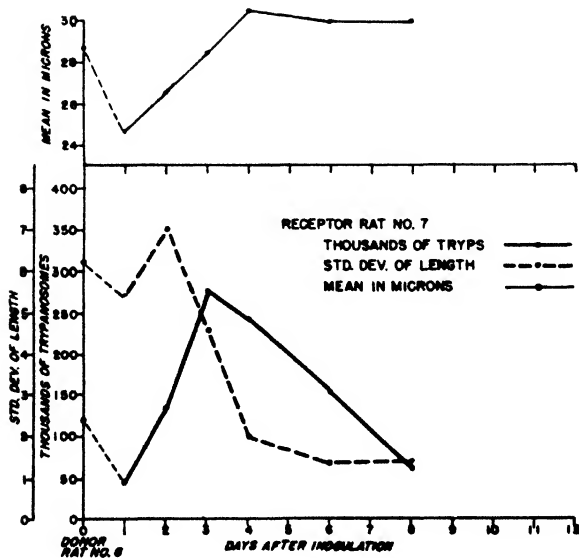


FIG. 6. Course of infection in receptor rat No. 7. (See explanatory notes under Fig. 1.)

TABLE 6  
Receptor Rat No. 6  
(Data as for Table 1)

Kind of Data	Donor Rat No. 5 5th day*	Receptor Rat No. 6—Days after inoculation					
		1*	2*	3*	4	6	8
Trypanosomes/1,000 . . . .	130	42	115	320	200	145	95
Std. Dev. . . . .	1.9	4.8	5.2	4.6	2.5	2.1	1.8
C. V. % . . . .	15.8	18.3	19.4	15.6	8.0	6.6	5.8
Mean in $\mu$ . . . .	30.7	26.0	26.6	29.4	31.3	31.5	31.0

Certain recovered rats (Nos. 8–15) were inoculated at the same time as each of the three normal rats, and with the same number of trypanosomes from the same donor rats. There were two along with receptor rat No. 5, three with r.r. No. 6, and three with r.r. No. 7. Wet and stained smears from these receptor rats were negative the day after inoculation and thereafter.

TABLE 7  
Receptor Rat No. 7  
(Data as for Table 1)

Kind of Data	Donor Rat No. 6 5th day*	Receptor Rat No. 7—Days after inoculation					
		1*	2*	3*	4	6	8
Trypanosomes/1,000 . . . .	120	48	135	380	215	155	65
Std. Dev. . . . .	6.2	5.4	7.0	4.6	2.0	1.4	1.4
C. V. % . . . .	21.4	21.8	26.3	16.2	6.5	4.5	4.7
Mean in $\mu$ . . . .	28.7	24.7	26.6	28.5	30.5	30.1	29.8

## DISCUSSION

The nature of the experimental data suggests that the discussion be developed first about proved phenomena, then about tentative conclusions based on the results and, finally, problems suggested for future investigation.

The fruitless attempts to reinfect eleven recovered and two near-recovered (i.e., still harboring adult trypanosomes) rats are recorded in the protocols of Series I and II. In these cases the donor rats were untreated, while the receptor rats were treated with salicylate. The negative results from these inoculations with reproducing trypanosomes and those with adult and reproducing trypanosomes mentioned in the introductory paragraph prove the improbability or reinfecting recovered and near-recovered rats under such circumstances. The possibility is not

absolutely precluded, however, because it was shown in the previous report (1) that intervention with salicylate in the fifth day of several infections, while dividing trypanosomes were still appearing, resulted in prolongment of the reproductive phase. Recently we have intervened in two rats on the seventh day, while dividing forms were still appearing, and with positive results. It is admittedly puzzling that failure to reinfect is the rule when dividing trypanosomes from untreated rats are introduced into treated recovered rats.

The aforementioned protocols also reveal that a certain number of salicylate-treated recovered and near-recovered rats became reinfected after they were injected with reproducing trypanosomes in diluted blood from treated donor rats. It is important to note that the trypanosomes were injected in large numbers, and that at the time of transfer the tempo of reproduction was high. The improbability of reinfesting untreated recovered rats by the same procedure is supported by (1) the negative results from eight tests in Series III, (2) frequent failure to reinfect even treated recovered rats, and (3) the well-known fact that rarely, if ever, can an untreated recovered rat be reinfected by injecting it with *T. lewisi* in any stage of its life cycle.

The course of the reinfection in receptor rat No. 4, which is recorded in Table 4 and charted in Figure 3, is clear-cut and understandable in the light of our knowledge of the course of a normal primary infection (cf. Taliaferro (2, 4)). At the time of transfer the standard deviation of  $4.1 \mu$  applied to the trypanosomes in the donor rat, but after a day in the receptor host the value declined to  $2.8 \mu$ , and after another day to  $1.4 \mu$ . A similar initial drop in the standard deviation was also noted in receptor rats Nos. 0, 1, 2, and 3. It did not occur in receptor rats Nos. 5, 6, and 7 which had experienced no previous infections. It is obvious that despite salicylate treatment of both donor and acceptor hosts the trypanosomes receive quite a jolt when transferred into the recovered host. It was possible by prolonged searching, however, to note actual division in rats Nos. 2, 3, and 4 during these early days when standard deviations were low, but none could be found in rats Nos. 0 and 1. The cause of the initial drop in standard deviation constitutes a problem for future investigation.

By the third day the standard deviation for the infection in rat No. 4 had risen sharply to  $6.1 \mu$ . Afterwards it remained high until it commenced the descent on the tenth day, three days after salicylate administration was discontinued. The trypanosome was definitely in the adult phase on the twelfth day and the counts became very low. They were entirely absent from the blood on the sixteenth day. Thus the reinfection in rat No. 4, like the typical primary infections charted by Taliaferro (2, 4), was characterized by the reproductive phase followed in due time by the adult phase. In the untreated rats, however, the duration of multiplication is limited to the minimum time required for the natural completion of a host reaction, while in the treated rat it is conditioned by the length of the course of treatment plus the time required for the host reaction. The continuation of multiplication several days after cessation



of treatment may be explained by the persistence of the drug in the blood and the time required for the reaction product to form after the drug level falls.

The chart for receptor rat No. 3 (Fig. 2, based on Table 3), which was dosed with the drug through the tenth day, presents a number curve very much in agreement with that for rat No. 4 considering the longer duration of dosing, but the curve for standard deviation, instead of continuing the drop of the thirteenth day, sharply rose again to a higher peak on the seventeenth day. It was on its way down again, however, when the infection became practically extinguished on the nineteenth day. A similar though much milder phenomenon occurred in rat No. 0.

Receptor rats Nos. 1 and 2 (Table 2) deserve special discussion. The first animal harbored adult trypanosomes at the time it was inoculated, and all of the flagellates were definitely of the adult type so far as extensive microscopic observation could determine. This was true through the second day after inoculation. But on the fourth, sixth, eighth, and eleventh days there were located in the smears a few definite examples of the large and small forms characteristic of the reproductive phase, though no examples of actual division of cell organelles were seen. The reproduction occurring in rat No. 2 was of the adult type previously discussed.

What would be the course of the infection in untreated rats without a record of previous infection if inoculated with enormous numbers of the flagellate in diluted blood from salicylate-treated donor rats? Series III was designed in large part to answer this question. The data for receptor rats Nos. 5, 6, and 7, recorded in Tables 5, 6, and 7, respectively, and presented graphically in Figs. 4, 5, and 6, definitely depict multiplicative phases of short duration. The parasite population had definitely attained the adult phase after four or five days. Here is further proof that the prolongment of reproduction in the recovered rats was due to the administration of salicylate to them rather than to the donor rats.

Why were most of the recovered rats refractory to reinfection despite salicylate treatment? Since the answer to this question must embody an assumption as to the nature of immunity to *T. lewisi* in the rat, whose controversial aspects were discussed in the former paper (1), the explanation offered here must be regarded as tentative. If the Taliaferroan doctrine of the formation of separate ablasic (anti-reproductive) and trypanocidal antibodies is correct, then the refractory animals may be regarded as possessing at testing time a trypanocidal titre too high for the introduced trypanosomes to endure, since the salicylate may be presumed to have neutralized most of the ablacin. Conversely, the animals successfully reinfected did not manifest sufficient trypanolytic titre to destroy the large numbers of introduced trypanosomes faster than they could multiply with the protection of the salicylate. Receptor rat No. 0 (Fig. 1) is an ideal example of a microorganism with near-borderline survival in the face of destructive forces, but bravely reproducing over a long period, and finally succumbing after the reproductive potential declined following the with-

drawal of salicylate. Rats Nos. 1 and 2 (Table 2) presumably were harboring more extreme but fundamentally similar reinfections.

The course of the infection in rat No. 3 (Table 3; Fig. 2) agrees with the above hypothesis, at least up to about the twelfth day. The chart might be interpreted to mean that up to that time the trypanosome was multiplying freely and the population was rising not exponentially, but in arithmetic progression. The latter implies casualties explainable by trypanocidal action. The number curve then fell precipitously until the sixteenth day, which is understandable; but standard deviations, after a decline on the thirteenth day, rose again until the seventeenth day, then commenced to decline.

Is it necessary to assume that in this case withdrawing salicylate released suppressed trypanocidal activity while reproduction continued unrestrained? It will be noted that in rat No. 4 (Fig. 3), drop in numbers after the ninth day was coincident with drop in standard deviation, as would naturally follow the assumption of increasing ablasic activity attended by more or less constant trypanocidal activity. The number decline on the ninth-tenth day from 325,000/mm.<sup>3</sup> to 65,000/mm.<sup>3</sup> amounted to a crisis. It was in evidence because the tempo of reproduction was decelerating.

The number decline in rat No. 3 from 738,000/mm.<sup>3</sup> to 50,000/mm.<sup>3</sup>, however, was of four days' duration instead of a single day, which is in agreement with what would logically be expected from the combination of a weaker innate trypanocidal mechanism and a parasite population that on this account had attained a greater peak. It should also be taken into account that the duration of salicylate treatment was three days longer in rat No. 3 than in rat No. 4, and that the mechanism of ablastin formation may have been more deeply affected than it was in rat No. 4. It is also possible that rat No. 3's intrinsic ability to form ablastin was weaker.

The curve for mean length and the fact that actual production was last observed in the smears on the tenth day indicate that after salicylate was withheld from rat No. 4 on the seventh day the production of the small types of trypanosomes (Plate A: 5 and 6) from the larger types (Plate A: 8, 1, and 3) slowed down drastically, and the circumstances of a peak for length on the tenth day and a number crises on the ninth-tenth day indicate the selective and efficient slaughter of the smaller types and the survival of the large type.

Actual reproduction, however, was observed in rat No. 3 up to the seventeenth, but not on the nineteenth day. The peak for mean length on the sixteenth day, the day before the last dividing form was seen, was not so high as that for rat No. 4, nor were its ascent and descent so precipitous, facts which are in accord with a less efficient and lethal trypanocidal mechanism. The last assumption is justified as well by the sharper rise in numbers in rat No. 3 as compared with rat No. 4 as by the slower decline. (Note: The scale of the ordinate in Figure 3 is twice

that in Figure 2.) It appears that it is really the survival of many of the smaller types along with the largest types and their very small progeny which is chargeable to less efficient trypanocidal action, that is responsible for the apparently anomalous standard deviation curve.

Positive results with new techniques usually suggest more problems than they solve, and the present instance is no exception. In the previous paper (1) it was suggested, as a working hypothesis, that the reaction-product which inhibits reproduction in *T. lewisi* infection is composed of a protein moiety in union with pantothenic acid. The reasons stated or implied were as follows:

1. Taliaferro's (5, 6) discovery of the protein nature of the product.
2. Our former work (7) showing that the anti-reproductive process was inhibited in rats on a pantothenate-deficient diet.
3. The previously reported results showing that the anti-reproductive process was inhibited also by the administration of sodium salicylate to the host.
4. The previous work of Ivanovics who noted inhibition of growth of *Staphylococcus aureus* in culture in the presence of sodium salicylate, and removal of the inhibition by the addition of pantothenic acid.
5. Citations to the literature wherein salicylates had been shown to play the role of inhibitor in the functions of certain other enzymes, namely, zymase, hyalouronidase, etiozymase, cocarboxylase (cf. von Euler (8)) and, hypothetically, the specific enzymes which enable bacteria to synthesize pantothenic acid.

The present report contributes the additional information that reproduction may recur in immune or near-immune rats following reinfection when a certain procedure utilizing salicylates is employed. Thus it might be assumed that the reaction product which inhibits reproduction, like many enzymes, can be broken down after it is formed. Further and more exhaustive testing of the hypothesis as to the nature of the antibody is also indicated.

In fact, the whole problem of the nature of immunity to *T. lewisi* infection needs reinvestigating. The interpretation of our results has been, admittedly, Taliaferroan. Augustine's (9) recent work wherein he stressed the phagocytosis of dividing and adult trypanosomes after agglutination may indeed be part of the picture in the normal immunizing process. Taylor and Becker (10) have discussed the occurrence of agglutination rosettes in infected normal rats and the presence of trypanosomes inside Kupffer cells of infected pantothenate-deficient rats. We have frequently noted agglutination in the blood of untreated rats; but never have we encountered it in infected rats under salicylate treatment, though there was incontrovertible evidence of the disappearance of trypanosomes from the blood.

Host-specificity of parasites is still largely in the realm of unsolved problems. Our success in meeting one phase of resistance with salicylate offers hope that other aspects of host resistance may be overcome by other drugs.

In the above discussion of the interpretation of the graphs, it was obvious that further study is needed of the significance of mean length and standard deviation in relation to each other and to the number curve. The salicylate treatment, which seems to practically eliminate the effects of the anti-reproductive mechanism on the reproductive cycle, should make possible a critical study of the course of infection wherein reproduction is unrestrained.

### CONCLUSIONS

1. Reinfection of recovered and near-recovered rats with *T. lewisi* is possible in certain cases—providing both the receptor and donor rat have undergone adequate treatment with sodium salicylate and the inoculation is made with a large number of trypanosomes in the multiplicative phase.

2. The reinfection is characterized by a multiplicative phase whose duration is dependent upon the length of the period of treatment.

3. Reinfections succeed when the reproductive potential released by the treatment exceeds the trypanocidal potential of the immune or near-immune host.

4. Conversely, refractoriness to reinfection in recovered rats is due to the destruction of trypanosomes faster than they can multiply.

5. Trypanocidal titre is extremely variable among recovered rats.

6. Clearing the blood of *T. lewisi* during recovery and immunity to reinfection would not be the universal rule if the trypanocidal mechanism of the host were not complemented by an anti-reproductive process.

7. The multiplicative phase in normal untreated rats injected with rapidly reproducing trypanosomes from salicylate-treated hosts is definitely limited by the host reaction and is of short duration.

8. The results obtained conform in general with the Taliaferroan theory of dual antibodies, but further investigation is suggested to compose this and the Augustinian points of view.

9. Success in breaking down one phase of host-resistance offers encouragement for a broader attack on the problem of the nature of host-specificity.

10. Adult trypanosomes may undergo fission in reinfections of recovered rats when the release from the anti-reproductive process is approximately the minimal for permitting reproduction and trypanocidal efficiency is only near maximal.

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# HISTOLOGICAL STRUCTURE OF THE STEM OF ZEA MAYS IN RELATION TO STIFFNESS OF STALK<sup>1</sup>

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The ability of corn plants to resist stem breakage is an important factor in the selection of lines for commercial production. The study of stem rots and the extension of the range of the corn borer in the Corn Belt in recent years have emphasized the desirability of selecting stiff-stalked corn varieties which undergo less breakage even when infected.

Factors that may contribute to stem strength are: the number of bundles in relation to stalk diameter, bundle area in relation to stalk diameter, the radial width of the epidermis, the radial width of the hypodermal sclerenchyma, the width of the band of lignified parenchyma extending inward from the hypodermis, and cell wall thickness in the foregoing tissues. The present study was designed to measure these structural features, to evaluate the importance of various strengthening tissues, and to develop methods for further studies of stalk strength.

## REVIEW OF PERTINENT LITERATURE

The development of the tissues of the bundle sheaths and the hypodermis of the maize stem has been described by Esau (2), who stated that the sheath is differentiated early in the course of bundle development. The peripheral cells divide anticlinally as the bundle increases in circumference. On the protozylem side and on the bundle flanks, the number of cell layers increases by periclinal divisions. Divisions both inside and outside the original sheath layer increase the thickness of the sheath at the protophloem side of the bundle. Esau points out the lack of developmental distinction between the bundle sheath and the adjacent tissues. A sheath cell may be the sister cell of a xylem element, or a sheath cell may be added by divisions of adjacent parenchyma cells. Hypodermal cells are initiated by longitudinal divisions of the subepidermal parenchyma. This process begins when the sheath at the protophloem side of the bundles is being thickened.

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Weaver (13) stated that three days after planting, vascularization consisted of provascular strands only. At fifty-eight days, vascular bundles were completely differentiated in all internodes halfway up the stem. Weaver also found that at maturity a given line of maize had a characteristic bundle size, at least in the lower two-thirds of the stem.

Weaver's findings agree with those of Hershey (6 and 7), who reported that the majority of the bundles are differentiated forty days after planting. The number of vascular bundles in the corn stalk ranges from 400 to 950, depending on the line, the stalk diameter, the height of the stem, and the age of the plant. Hershey found a significant correlation between the diameter of the stalk and the number of vascular bundles. The number of bundles in the rind or lignified area is approximately one-half the total number of bundles in the stem. The vascular elements in the smaller peripheral bundles are reduced in size and number.

The relation between stem histology and stem strength has been studied in several important grasses. In the literature on the subject, several different views of the value of histological features as an index of lodging resistance are represented. Divergent opinions are also held with respect to mechanical methods of testing lodging resistance.

A histological study of stalk-breaking in maize was made by Hunter and Dalbey (8) in an attempt to find a method of anticipating stalk weakness in inbred lines. Studies made at various stages in the life of the plant showed that the stalk of the nearly mature plant was the most satisfactory for examination of the tissues that contribute to stalk strength. Young plants showed no consistent significant differences which correlated with stalk-breakage in the mature plant. Thick bundle sheaths, thick-walled sub-epidermal sclerenchyma, and angular, close-fitting cells characterized stiff-stalked lines. Thin walls, narrow bundle sheaths, and large intercellular spaces were consistent features of weak stalks. In general, histological structure gave an accurate indication of the relative degree of stalk-breakage in the field.

McRostie and MacLachlan (10) found that in some maize hybrids the extent of lignification beyond the rind and the number of vascular bundles within this lignified area were definitely correlated with lodging resistance. Tests were made to determine the resistance of the internode to breaking, crushing, and penetration. The crushing response was correlated with lodging resistance.

Khanna and Panje (9) investigated the anatomy of the sugar cane stalk in relation to rind-hardness. Rind-hardness was determined by puncturing the second joint above ground level. The number of vascular bundles per unit area and the degree of lignification of the rind parenchyma and of the sheath cells were found to be the most important indicators of hardness. The term "bundle complex" was used to include the number, size, and degree of lignification of the vascular bundles. Lignification of the sheath did not contribute to stiffness when not accompanied by lignification of the parenchyma cells between the outer rows of bundles.

Histological investigations of the culms of small grains have been somewhat more extensive than studies on corn. Moldenhawer, as cited by Garber and Olsen (3), studied wheat and barley and found that there was less lodging in stems that had more vascular bundles. Garber and Olsen also quoted the work of Albrecht, who accepted breaking strength as a lodging index, and found correlations in winter wheat between breaking strength and the weight of straw, total area of a cross section of the vascular bundles, and thickness of culms. Albrecht found little correlation between lodging and the thickness of the sclerenchyma.

Contrary to these early reports, Garber and Olsen (3) found that in barley no marked relation occurs between lodging and average culm diameter, average thickness of culm wall, average total area of bundles, or average area of sclerenchyma near the periphery of the culm. A correlation between lodging and the thickness of sclerenchyma cell walls was reported in oats but not in barley. Stiff-stalked plants of spring wheat had more bundles, more sclerenchyma, and a higher total bundle area than did the weak stalks. The reverse was found to be true of winter wheat. Percival (11) related straw strength in wheat chiefly to the thick, lignified walls of the hypodermis.

In oats and wheat, Welton and Morris (14) associated lodging with hypernutrition, which produced low dry matter content, thin-walled cells and a narrow zone of hypodermal tissue. Lodging was found to be prevalent when there was a preponderance of vegetative growth.

Ramiah and Dharmalingam (12) studied lodging in rice and found no relation between lodging and the number and size of the vascular bundles, the size of air spaces, or the thickness of the layer of sclerenchyma on the inner sides of the bundles. Erect plants had a greater internodal diameter and thicker culm walls. The authors concluded that no single factor can be used as an index of lodging-resistance.

Brady (1) studied three varieties of oats representing extremes of lodging susceptibility. The strongest straws had more bundles, a wider band of thick-walled, lignified tissues, and thicker sclerenchymatous cell walls than did the intermediate and weak lines. However, sclerenchyma wall thickness was the only character that showed a consistent relation to culm stiffness. Wide spacing of plantings seemed to produce characteristics associated with lodging resistance. On the basis of these results Brady concluded that no histological character could be taken as an absolute index of lodging resistance. Brady also stated that external features of the lower internodes furnish as good evidence of lodging-resistance as measurements of internal features.

Hamilton (4) reported that in oats the most reliable criteria of lodging were plant height, culm diameter at the second internode, and the size and number of vascular bundles. Many characters which were regarded by other workers as possible lodging indices were found by Hamilton to show inconsistent correlations with lodging susceptibility. Some unreliable characters were the width of the sclerenchyma layer and the width of culm walls. The most clear-cut lodging index was the number



of bundles in the parenchyma area, which was much greater in strong straws than in weak.

#### MATERIALS AND METHODS

The plants used in this study were obtained from the Agronomy Department of Iowa State College. The lines were L289; L289(B2), a recovered strain of L289 having Indiana B2 as the nonrecurrent parent; 507, a five generation line isolated from a stiff-stalk synthetic; (WF9 x D17)-561, a five generation inbred isolated from a single cross involving WF9 and Doubit 17.

Stalk-stiffness was estimated on the basis of field behavior over a period of years, as judged by experienced field workers. L289 is weak-stalked. L289(B2), 507, and WF9 are classed as having stiff stalks. Dr. G. F. Sprague proposed the use of L289(B2) in this study because of its relative resistance to lodging when infected by *Diplodia zeae*.

Ten well-developed plants of L289 and five plants of the other three lines were collected September 24, 1945. Three transverse sections about one-fourth inch thick were cut from the first free internode, the first internode that was not anchored by prop roots. Three sections were also taken from the second free internode. These sections were fixed in F. A. A.

Segments approximately one-eighth of the stalk area were cut from each of the three first internode sections and dehydrated in an ethyl alcohol-normal butyl alcohol series, with frequent aspiration. Normal butyl alcohol containing 5 per cent chloroform was used as the wax solvent. The tissues were infiltrated with Parawax and embedded in Tissuemat.

The embedded blocks were prepared for sectioning by soaking in water at 35° C. for twenty-four hours. Cross sections were cut fifteen microns thick, and stained in hemalum and safranin.

Measurements were made with a 7.5x eyepiece micrometer and 10x and 45x objectives. Twenty bundles were measured in the rind of each plant of a collection to determine the average bundle size for each line. The following measurements were made for each plant:

1. radial and tangential diameters, including the sheath, of ten vascular bundles in the rind;
2. radial and tangential diameters of ten sheath cells and cell lumens;
3. width of the hypodermal zone and number of cells in ten random areas;
4. radial and tangential diameters of ten hypodermal cells, ten epidermal cells, and ten parenchyma cells of the rind, and of cell lumens;
5. five random measurements of the width of the band of lignified tissue extending inward from the epidermis through the lignified parenchyma.

The percentage of the cell wall per cell was calculated from the formula employed by Hanson (5) in her work with fibers.

Stalk diameter measurements were obtained from the first internode in all the plants of the four lines studied.

Projection drawings of sections were made at a magnification of approximately 27x. The number of vascular bundles in comparable areas of the stem was determined by counting the bundles in a segment based on a fifteen degree angle at the stalk center and extending inward from the epidermis one-fourth of the radius of the stem. This segment was designated Area I and covered approximately 1.8 per cent of the total stalk area. Area II, which was included in Area I, extended inward from the epidermis only one-eighth of the stalk radius and covered approximately 1.0 per cent of the stem area. Area II included only rind, while Area I also included some pith.

The bundle area and bundle number per unit area were determined by making projection drawings on 1 mm. squared paper. A sample of each sheet was weighed for use as a standard. The cutout Areas I and II were weighed. The bundles were then cut out of Area II and weighed. Finally, the bundles from the entire segment of Area I were weighed. Bundle number per square millimeter and percentage of bundle area per section were calculated by the method described by Weaver (13). He stated that although areas computed in this manner were not very accurate as absolute values, they appeared valid for use in comparing lines.

The percentage of bundle sheath per bundle was found by making drawings with a micro-projector at a magnification of 120x. Three groups of three successive bundles from the epidermis inward were measured. Measurements of total bundle area and the area of vascular tissues in the bundle were made with a planimeter.

The total number of bundles per section was found by cutting thin sections one-sixteenth of the stalk area and counting the bundles present.

Preliminary observations were made on a few lines obtained from the Pioneer Hi-Bred Corn Company, in particular the weak-stalked line A99 and two stiff-stemmed Jalisco flints. ✓

#### OBSERVATIONS

Data on stalk breakage were obtained from field trials conducted by the corn breeding project over a period of years. Line L289 has been ranked as susceptible to breakage. The other three lines—L289(B2), 507, and WF9—are ranked as resistant to stalk-breakage.

In the collections made for the present study the average stalk diameter of the first free internode was found to be greatest in line 507. WF9 ranked next and L289(B2) and L289 showed little difference in average stalk diameter (Table 1).

The weakest-stemmed line, L289, had the highest bundle number. The stiffest line, 507, had the smallest number at the first free basal internode.

The percentage of bundle area was determined in two areas previously described as Area I and Area II. L289 ranked highest in the percentage of bundle area per section (Table 1).

The number of bundles per square millimeter was also determined in the designated two areas. L289 had the highest number of bundles per square millimeter in Area I. L289 (B2) had the highest number of bundles

per square millimeter in Area II (Table 1). There was a significant difference in the number of bundles per square millimeter between 507 and WF9 and between these lines and L289 and L289(B2). There was no significant difference in bundle number per square millimeter between L289 and L289 (B2).

TABLE 1  
DIMENSIONS OF STALK IN RELATION TO BUNDLE NUMBER AND RELATIVE BUNDLE AREA

Line	Average Stalk Diameter in cm.	Bundles per Section	Per Cent Bundle Area		Bundles per mm. <sup>2</sup>	
			Area I	Area II	Area I	Area II
L289 (Weak) . . . . .	2.3	774.1	24.93	30.28	3.93	5.24
L289 (B2) (Stiff) . . . .	2.2	696.8	21.32	27.33	3.90	5.45
507 (Stiff) . . . . .	3.5	624.0	18.96	23.52	1.62	2.09
WF9 (Stiff) . . . . .	3.0	736.0	18.38	21.32	2.38	3.57
Least significant difference, 5 per cent level					0.62	1.03

The histological details of the maize stem are too well known to require detailed description here. The arrangement of bundles in relation to the epidermis and hypodermis is shown in Figures 1-4. Enlarged details of the tissues that contribute most to stalk stiffness are shown in Figures 5 and 6.

Microscopic observations indicate that 507 is strikingly different histologically from the other three lines. The vascular bundles are larger and the cell walls are lignified throughout the section (Fig. 4). This contrasts especially with L289 and L289 (B2) which have clearly delimited bands of unligified parenchyma at the stalk periphery (Figs. 1 and 2). Line 507 has no continuous band of unligified parenchyma adjacent to the hypodermis, such as is found in the other three lines.

L289 and L289 (B2) are similar histologically. The cell walls in the rind are not greatly thickened in these two lines. WF9 is similar to L289 and L289 (B2) with respect to the width of the lignified zone, but in WF9 the cell walls in this zone and in the bundle sheaths are very thick (Figs. 3, 5, 6).

TABLE 2  
DIMENSIONS OF BUNDLES AND RELATIVE PERCENTAGES OF BUNDLE SHEATH (SCLERENCHYMA)

Line	Bundle Dimensions in mm.		Per Cent Sheath per Bundle	Per Cent Sheath per Section
	Radial	Tangential		
L289 (Weak) . . . . .	.24	.23	67.72	15.88
L289 (B2) (Stiff) . . . .	.22	.22	69.05	14.72
507 (Stiff) . . . . .	.42	.35	78.49	14.88
WF9 (Stiff) . . . . .	.26	.28	70.09	12.08

Three of the lines did not exhibit much difference with respect to bundle size, but 507 had markedly larger bundles. L289 had the highest percentage of sheath per section (Table 2).

The rind is defined here as the tough zone that includes the epidermis,

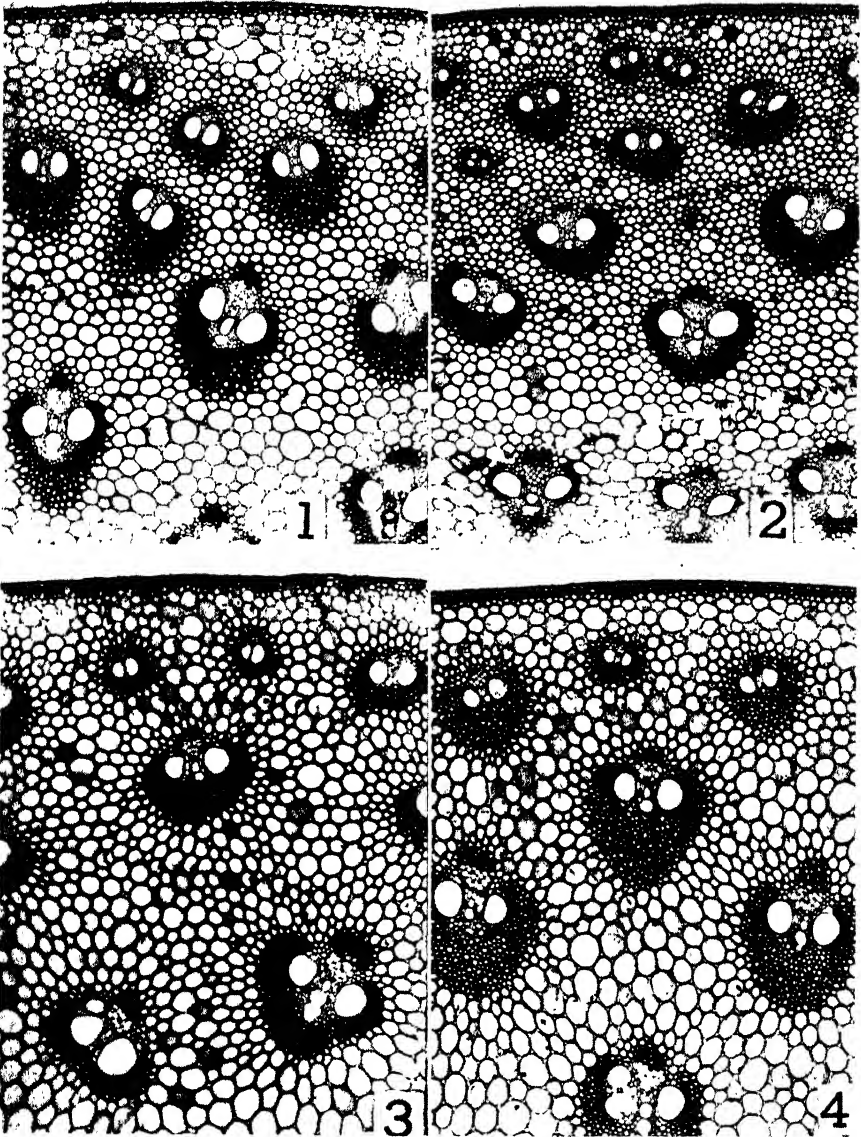


FIG. 1. Cross section of stem of maize, line L289. 48x.

FIG. 2. L289 (B2).

FIG. 3. Line WF9.

FIG. 4. Line 507.

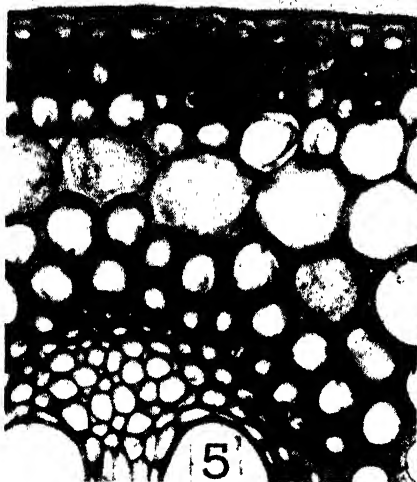


FIG. 5. Details of epidermis and sub-epidermal tissues of WF9. 320x.

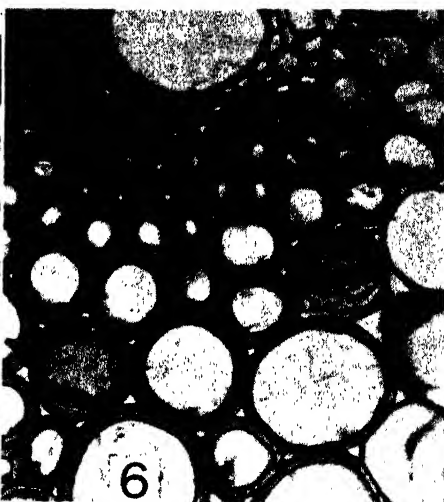


FIG. 6. Detail of margin of a bundle and adjacent tissues of WF9. 320x.

hypodermis, and all vascular and nonvascular tissues through the lignified portions of the pith parenchyma. Lines 507 and WF9 had significantly thicker rind and hypodermis. Only line 507 had a significantly thicker epidermis, and the number of cell layers comprising the hypodermis was significantly different between L289(B2) and WF9 (Table 3).

TABLE 3  
THICKNESS OF COMPONENTS OF THE "RIND"

Line	Thickness of "Rind" in mm.	Thickness of Hypodermis (microns)	Thickness of Epidermis (microns)	Layers of Cells in Hypodermis
L289 (Weak) . . . . .	1.13	21.23	14.53	1.9
L289 (B2) (Stiff) . . . .	1.21	17.77	13.95	1.7
507 (Stiff) . . . . .	2.57	26.53	16.45	1.9
WF9 (Stiff) . . . . .	1.49	31.42	14.02	2.2
Least significant difference at 5% level.	0.19	4.82	1.40	0.29

Cell wall thickness showed no consistently significant correlations in the four lines. Epidermal cell walls showed significant differences only between WF9 and L289 (B2). The stiff-stalked line WF9 had significantly thicker cell walls in hypodermis, sheath, and parenchyma. (Table 4.)

In each of the four tissues listed in Table 4, WF9 showed a consistently higher percentage of cell wall per cell than the other three lines. Only WF9 differed significantly from the other three lines in cell wall percentage in the epidermis. In the sheath cells and in the parenchyma there

were significant differences in percentage of cell wall between all lines but L289 and L289 (B2). The hypodermis of WF9 was not significantly different from that of the other lines.

TABLE 4  
CELL WALL THICKNESS AND PERCENTAGE OF CELL WALL PER CELL

Line	Cell Wall Thickness in Microns				Per Cent Cell Wall per Cell			
	Epidermis	Hypodermis	Sheath	Parenchyma	Epidermis	Hypodermis	Sheath	Parenchyma
L289 (Weak)	3.11	3.79	3.63	2.91	63.38	77.20	69.77	28.95
L289 (B2) (Stiff)	2.99	3.20	3.52	2.05	56.97	82.49	71.01	28.64
507 (Stiff)	3.54	3.51	2.76	2.74	57.52	68.57	18.81	19.19
WF9 (Stiff)	3.95	5.17	5.76	5.22	71.74	88.79	88.16	17.79
Least significant difference at 5 per cent level.	0.73	0.68	0.91	0.98	8.36	7.13	4.62	7.13

## DISCUSSION

The present study was limited to the peripheral regions of the stem. Preliminary observations showed that the interior tissues of the stalk are only slightly lignified in most lines, and the bundle sheaths are narrow and thin-walled. The parenchymatous pith probably contributes little to the strengthening of the stalk. The rind, on the other hand, is characterized by thick-walled parenchymatous cells and small bundles with large, thick-walled sheaths.

In the two peripheral areas described earlier, the relation of bundle number to stalk strength is nearly identical. Bundles per square millimeter and percentage of bundle area per section are somewhat higher in the outer eighth of a sector than in the outer fourth. The lodging-resistant stalks have the lowest percentage of bundle area per section. WF9 and 507 are very similar in percentage of bundle area per section.

WF9 and 507 have the lowest number of bundles per square millimeter in both areas. There is little difference in bundle number per square millimeter in L289 and L289 (B2).

High bundle number is not consistently related to stalk strength in corn, as shown by L289, a weak-stalked line, which has the greatest number of bundles in the first free internode, whereas breakage-resistant line 507 has the lowest bundle number, and WF9 is intermediate between L289 and L289 (B2).

Bundles in 507 are considerably larger than those of the other lines. This explains the fact that although 507 has a low total bundle number, its percentage of bundle area per section is equal to that of WF9.

Hamilton (4) found that the radial diameters of vascular bundles in strong varieties of oats were significantly greater than in weak-stalked lines. Width of bundles did not show a significant variation between

weak and strong plants. In the corn plants examined, bundles in stiff stalks—with the exception of L289 (B2)—have greater radial diameters and are wider than the bundles in weak-stalked plants. However, the size difference is significant only in line 507.

Stalk diameters, which were found by other workers to be correlated with lodging in all grains studied except barley, are larger in stiff-stalked lines WF9 and 507. L289 (B2) has a slightly smaller stalk than does weak-stalked line L289. Hershey (6) reported that in the material he studied, bundle number was highly correlated with stalk diameter. In the present study, line 507, with the greatest stalk diameter, has the lowest bundle number. WF9, which has a stalk diameter considerably greater than those of L289 and L289 (B2), ranks between these lines in total bundle number.

Closely associated with bundle number and bundle area is the percentage of sheath per bundle. The stiff-stalked lines have the highest percentage of sheath per bundle. L289, although somewhat lower in percentage of sheath per bundle than other lines, is still highest in percentage of sheath per section, due to the high percentage of bundle area per section. Stalks of 507 have a high percentage of sheath per bundle and rank second in percentage of sheath per section. WF9 stalks are not appreciably higher in percentage of sheath per bundle than L289, and stalks of WF9 have the lowest percentage of sheath per section.

The thickness of cell walls in the sheath is an important factor in determining the strengthening qualities of the sheath. The very thick sheath cell walls of WF9 probably compensate for the low percentage of sheath per section. In 507 the sheaths are large, but the cell walls are thin. Sheath cell walls of 507 are thinner than those of L289 and L289 (B2). This does not agree with the conclusions of Hunter and Dalbey (8), who found sheath cell walls thicker in stiff-stalked lines than in the weak-stalked lines.

In wheat, oats, sugar cane, and corn the thickness of cell walls in hypodermis, sheath, and parenchyma was found to correlate with stiffness of stalk. In the present study, cell walls did not show a consistent relation to stalk strength. 507 has thinner cell walls in sheath, hypodermis, and parenchyma than does L289. The extremely thick cell walls of WF9 are one of that line's outstanding features. WF9 has the highest percentage of cell wall per cell in the above tissues. Percentages of cell wall per cell do not correlate with stalk strength.

The area of hypodermal sclerenchyma was found to correlate with lodging in spring wheat, sugar cane, and winter wheat. No such correlation was found in barley, rice, and oats. In the four lines of corn studied, the width of the hypodermal zone does not correlate with stalk-stiffness. The strong-stalked lines 507 and WF9 have a broader zone of hypodermal tissue and a somewhat greater number of hypodermal cells than the other two lines. L289 (B2), however, has a narrower hypodermal zone than does L289. The radial width of the epidermal cells does not show a consistent relation to stalk strength. WF9 is intermediate in epidermal width between L289 and L289 (B2). Line 507 has a considerably wider epi-

dermis than the other three lines, and also a much wider total lignified area. The extent of lignification of parenchyma cells, even in the pith, is one of the striking characteristics of line 507. In measuring this zone, the inner limit of the lignified tissue was set at the point where parenchyma cells show an appreciable decrease in the density of the safranin stain. The extent of lignified tissue shows a consistent relation to lodging in the other three lines.

In the group of ten Pioneer lines on which preliminary examinations were made, A99, a weak-stalked line, had the highest number of vascular bundles per square millimeter and the thinnest cell walls in most tissues. The Jalisco flints, two of the stiff-stalked lines, had the lowest bundle number per square millimeter, and they had thick-walled cells and a wide zone of hypodermal sclerenchyma. The more contrasting lines merit further study with adequate samples.

#### SUMMARY

Four lines of maize were examined to determine the correlation between histological characters and stalk-stiffness. Line L289 is weak-stalked. The other three lines, L289(B2), 507, and WF9, are classed as stiff-stalked on the basis of observations of stalk-breakage in the field.

L289(B2) does not appear to differ morphologically from L289. The non-breaking quality of the stalk of L289(B2) is attributed to resistance to *Diplodia* damage.

The stiff-stalked lines 507 and WF9 have the greatest stalk diameter of the four lines.

The lignified "rind," which extends from the epidermis through the lignified zone of pith parenchyma, was found to be significantly wider in the stiff-stalked plants.

Weak-stalked plants have the highest percentage of bundle area and the highest number of bundles per square millimeter in the rind.

The percentage of sheath per bundle is greatest in the stiff-stalked plants. However, weak-stalked line L289 has the highest percentage of sheath per section.

Cell wall thickness in the epidermal cells is associated consistently with stalk-stiffness in 507 and WF9. No correlation was found between stalk-stiffness and cell wall thickness in sheath, parenchyma, and hypodermal cells. Percentage of cell wall per cell does not correlate with stalk strength in any of the foregoing tissues.

The stiff-stalked lines, except L289(B2), have a significantly wider band of hypodermal sclerenchyma. The number of layers of hypodermal sclerenchyma cells from the epidermis to the parenchymatous tissue is not consistent with stalk-stiffness.

Radial width of the epidermis is not consistently related to stalk strength.

Morphological characters that show a consistent relation to stalk strength are a low bundle number per square millimeter in the rind, a high percentage of sheath per bundle, a large stalk diameter, and a wide



lignified zone. Stalk stiffness is probably determined by a combination of morphological characters, interacting with pathological factors.

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# RUNOFF WATER AS AN AGENT IN THE LOSS OF SOLUBLE MATERIALS FROM CERTAIN SOILS<sup>1</sup>

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Plant nutrients and other solutes are lost from agricultural soils in several ways: harvested crops, organic solutes, and nitrogen by oxidation and denitrification; organic and inorganic solutes in drainage water as a result of soil leaching, and solutes in runoff water. These losses may or may not be accompanied by a proportionate loss of soil.

The removal of plant nutrients and other soluble materials from soil in runoff water has been studied less extensively than have the other types. Some analyses are available on seasonal composite samples of runoff water which furnish valuable but limited data on the amounts of soluble material that may be lost therein (8) (11), and some information is available from the analyses of individual runoffs (20). The specific causes of variation in the amount and concentration of solutes in runoff, therefore, have been largely a matter of conjecture. In the present investigation individual runoffs have been analyzed in order to determine more exactly these causes of variability.

An attempt has been made in the present study also to compare solution losses occasioned by runoff with those occurring as the result of leaching. It seems obvious that such a comparison should be made. Most lysimeters, however, have been constructed to eliminate runoff (19). Similarly erosion and runoff experiments are not ordinarily equipped to collect drainage water, nor were the field installations in the present investigation so equipped. However, a less satisfactory alternative was available. Soils of the type on which the erosion plots at the New York Agricultural Experiment Station at Geneva are located have previously been used in well-known lysimeter investigations, the results of which may therefore be assumed to bear a relationship to the present study. Ontario loam soil (heavy phase) was used in the Geneva lysimeter studies of Collison *et al.* (5) (6), and the closely associated Dunkirk silty clay loam was used in part of the lysimeter investigations of Lyon, Bizzell, *et al.* (2) (23).

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## REVIEW OF PREVIOUS WORK

A search of the literature shows that few independent investigations have been made of solutes in runoff water.

Duley reports the analysis of composited samples of runoff water collected over a one year period from erosion plots of the Missouri Agricultural Experiment Station (11) (25). He found that calcium and sulphur were lost in larger amounts than any of the other elements determined. The loss of potassium was relatively small, but in some cases amounted to more than would ordinarily be applied in commercial fertilizer. The losses of magnesium, sodium, and phosphorus were too small to be of practical agricultural significance, and those of nitrogen were not great.

Daniel, Elwell, and Harper (8) determined the nitrate nitrogen content of runoff water from the Vernon fine sandy loam soil of the control erosion plots at the Soil Conservation Service Experiment Station at Guthrie, Oklahoma, during the period 1930-37. Annual averages of the amounts lost ranged from 1.19 pounds per acre from a desurfaced plot in continuous cotton to 0.01 pounds per acre from a virgin woods plot. The quantity of nitrate nitrogen removed in runoff water was more closely related to the percentage of runoff than to the amount of soil lost. Daniel found that the average annual nitrate nitrogen in rainfall, 0.98 pounds per acre, was considerably greater than that removed by runoff water from all plots except the desurfaced area, and concluded that nitrate nitrogen is not removed from the surface of that particular soil in large amounts by erosion.

Keiller, in Ceylon, determined losses of ammonium sulphate in runoff water from a rubber plantation during rains at varying times after fertilizer application (16). Plots were laid out on red laterite soil of moderate slope and were fertilized with ammonium sulphate at the rate of 448 pounds per acre. His work on desurfaced hard fallow covered a period of 34 days. During this time, six heavy showers of high intensity and relatively short duration occurred, with intervening periods of dry, hot, windy weather. The net equivalent of 1.15 pounds of ammonium sulphate per acre was lost from four of the six runoffs. On other plots on reasonably well forked rubber land, Keiller reports even smaller losses of ammonium sulphate. He concluded that "little loss of ammonium sulphate takes place by surface wash even from unforked and very hard laterite soil unless the runoff is very rapid." The rate of runoff appeared to be the important factor.

Kohnke (20) and Hickok (21) report analyses of runoff water from soils at Purdue Agricultural Experiment Station, Lafayette, Indiana, but their data are not directly comparable with the results of this study. They used watersheds of varying size, all more than one acre in area; runoff water samples were collected at first manually at given intervals during a runoff, and later by an automatic aliquot runoff sampler. The runoff water appeared to include indeterminate proportions of subsurface seepage and percolate waters. Finally, their samples were first digested with

hydrochloric acid on a steam bath before filtration so that the filtrate used for analysis included both exchangeable and dissolved ions. Losses in runoff would logically be expected to considerably exceed those found in this study despite the similar nature of the soils at both stations.

#### OUTLINE OF INVESTIGATION

Chemical analyses were made of approximately 185 separate runoff water samples from eight erosion plots. The samples were aliquots of all of the thirty-nine rains or thaws that caused runoff during the thirteen-month period March 1, 1938, to March 31, 1939, inclusive. As soon as possible after each rain or thaw an aliquot of the runoff from each plot was collected and then filtered through Pasteur-Chamberland filter candles under suction.

The filtrate was always clear and non-opalescent, although occasionally of yellowish hue due to organic solutes. It was assumed to contain only solutes in approximately true solution. Therefore, it was expected that the amounts of soluble materials present would be less than those reported where the filters used might have been coarser or where the water samples had been treated before filtration.<sup>4</sup>

Filtration usually required from 2 to 12 hours for completion. In a few cases the runoff water remained in contact with the soil it contained for more than 24 hours. Previous investigations of the soil solution (3) (4) (24) (28) show that the longer periods of contact of soil and water did not materially affect the concentrations of solutes in solution. The conclusion was supported in the present investigation by a series of conductivity measurements (9).

The total volume of runoff water was measured at the tanks in connection with a concurrent investigation of soil and water losses.

In preparation for analysis, the main body of the filtrate, 1,000 to 8,000 ml., was reduced by evaporation in large beakers to about 50 ml. The concentrate was then transferred to a platinum dish to be dried, weighed, and ignited. Most determinations were made on the ignited residue. A complete transfer, including the viscous coating that tended to accumulate on the beaker bottom, usually required the use of a few drops of hydrochloric acid. Frequent effervescence at this point indicated the presence of carbonates and bicarbonates, as would be expected in runoff water from soils derived from calcareous glacial parent materials.

In general, standard methods of analysis were used (1) (26). Calcium, magnesium, sulphur, and potassium were determined gravimetrically. Sodium was determined only approximately by difference from the weight of the double chlorides of sodium and potassium.

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<sup>4</sup>Duley (11) removed suspended material from the runoff water samples by clay filters. Daniel *et al.* (8) flocculated the suspended matter with copper sulphate and sodium hydroxide. Kohnke (20) states that runoff samples received concentrated hydrochloric acid up to one per cent volume and were then digested on a steam bath in order to flocculate the colloids and to replace the cations so that the exchangeable ions could be included with the dissolved ions; the solids were then filtered off.

TABLE 1  
CROPPING AND TREATMENT OF GENEVA EROSION PLOTS

	Ontario Loam, Slope 8 Per Cent to Northeast					Dunkirk Silty Clay Loam, Slope 5 Per Cent to Southeast		
	Plot 1	Plot 2	Plot 3	Plot 4	Plot 5	Plot 6	Plot 7	Plot 8
Cover.....	Red clover	Winter rye to May 18; sum- mer fallow to Oct.	Alsike clover	Soybeans sown broadcast	Fallow	Bluegrass	Fallow	Sweet corn af- ter alfalfa
Planting date...	.....	September 30	.....	June 6	.....	.....	.....	June 9
Growth.....	Fair	Fair	Weedy	Good	.....	Good	.....	Good
Spading date...	.....	May 18	.....	May 26	April 20	.....	April 20	April 27
Cultivation dates.....	.....	May 19; June 7, 24; July 14; Aug. 4, 23; Sept. 29	.....	.....	May 19; June 7, 24; July 14; Aug. 4, 23; Sept. 30	.....	Apr. 28; May 17, 31; June 23; July 20; Aug. 3, 22; Oct. 3	Apr. 28; May 17, 31; June 9, 20; July 6, 20; Aug. 3
Fertilization Rate.....	.....	5-10-5 500 lbs./acre	.....	5-10-5 500 lbs./acre	5-10-5 500 lbs./acre	.....	.....	5-10-5 500 lbs./acre
Date applied..	.....	June 7	.....	June 6	June 7	.....	.....	June 9
Prior fertili- zation.....	.....	5-10-5 annually, 1935-37	.....	5-10-5 annually, 1935-37	5-10-5 annually, 1935-37	.....	5-10-5 annually, 1936-37	.....
Prior cover.....	Red clover	Winter rye, summer fal- low	Alsike clover	Soybeans; stalks left over winter	Fallow	Bluegrass	Fallow	Alfalfa

Total nitrogen was determined by a modification of standard procedures (10) (12). A 400 ml. aliquot of the runoff water filtrate was placed in a Kjeldahl flask and rendered alkaline with 3 ml. of 35 per cent sodium hydroxide. About 0.5 gms. of Devarda's alloy and a small piece of paraffin were added. The ammonia already present and that resulting from the reduction of nitrates was distilled into 50 ml. of boric acid solution. A low flame was used in order to secure the greatest possible distillation of ammonia with the least distillation of water. The boric acid was then set aside and reserved for the later main distillation. After the preliminary distillation the contents of the flask were acidified with about 3 ml. of concentrated sulphuric acid and reduced in volume by further distillation to about 75 ml. At this point a regular Kjeldahl procedure was adopted. The resultant ammonia was distilled into the reserved boric acid, and subsequently titrated.

#### DESCRIPTION OF PLOTS

The plots used in this study are located at the New York State Agricultural Experiment Station and were originally installed in 1935 to determine the effects of various types of cover and treatment on erosion losses. Continuous records of rainfall, and of soil and water lost, had been kept since 1936. The eight plots, each 72.6 x 6 feet, are in two series, one a group of six plots on Ontario loam, and the other of two plots on Dunkirk silty clay loam. A border of about 6 feet around each plot is maintained under the same cover and treatment as that plot. All plots are similarly equipped to intercept and collect all soil and water lost. Cropping and treatment of the individual plots are outlined in Table 1.

#### DESCRIPTION OF SOILS

The two soil types of the Geneva erosion plots are representative of much of the Ontario Lowland Belt and Finger Lakes Region in New York. The Ontario soil is typical of those derived from calcareous glacial till, while the Dunkirk soil is typical of those derived from heavy calcareous glacial lake deposits. The two soils occur in closely associated patterns throughout much of the Ontario Lowland, with the Ontario soil occupying the higher lying knolls and hills, and the Dunkirk soil occurring in the lower lying intervening areas. The soil profile in both cases is that of immature gray-brown podzolic soils and represents the nearest normal profile development in the region. Drainage is good in the Ontario loam and good to imperfect in the heavier, more compact, and less pervious Dunkirk silty clay loam.

The Ontario loam profile has developed, since the retreat of the Wisconsin ice sheet, to a point where carbonates have been removed to a depth of two feet or more. However, the soil retains a relatively high calcium content, and is considered one of the most productive of New York soils.

The Dunkirk silty clay loam profile has undergone a somewhat greater removal of carbonates in its development than has the Ontario

TABLE 2

MONTHLY PRECIPITATION AT GENEVA, NEW YORK, JANUARY, 1938, TO MARCH, 1939

ONTARIO GAUGES*				DUNKIRK GAUGES*				
	Precipitation (inches)	Deviation from 43 yr. average (percentage)	Rain (inches)	Snow (water equiv.) (inches)	Precipitation (inches)	Deviation from 43 yr. average (percentage)	Rain (inches)	Snow (water equiv.) (inches)
1938: January . . .	1.66	-25.2	0.88	0.78	1.67	-24.8	0.88	0.79
February . . .	2.96	+53.4	1.82	1.14	2.82	+46.1	1.68	1.14
March . . .	1.80	-20.7	1.66	0.14	1.70	-25.1	1.55	0.55
April . . .	2.90	- 1.7	1.12	1.78	3.06	+ 3.7	1.13	1.93
May . . .	2.20	-32.9	2.20	...	2.54	-22.6	2.54	...
June . . .	2.76	-28.1	2.76	...	2.92	-24.0	2.92	...
July . . .	3.12	+ 1.3	3.12	...	3.32	+ 7.8	3.32	...
August . . .	5.55	+69.7	5.55	...	5.28	+61.5	5.28	...
September . .	4.17	+53.3	4.17	...	3.83	+40.8	3.83	...
October . . .	0.33	-88.6	0.33	...	0.29	-90.0	0.29	...
November . .	1.87	-31.0	1.56	0.31	1.75	-35.4	1.40	0.35
December . .	0.86	-63.6	0.57	0.29	0.66	-72.0	0.45	0.21
1939: January . . .	2.30	+ 3.6	0.14	2.16	2.30	+ 3.6	0.14	2.16
February . . .	2.49	+29.0	0.47	2.02	2.49	+29.0	0.47	2.02
March . . .	2.58	+13.7	1.44	1.14	2.58	+13.7	1.44	1.14
April, 1938 to March, 1939	31.13	...	23.43	7.70	31.03	...	23.22	7.81

\* Average of one recording and one standard gauge at plots.

loam. Profile development has been slow, due to the heavy compact nature of the calcareous lacustrine parent material. The soil is fairly high in natural productivity.

#### PRECIPITATION AND WEATHER CONDITIONS

Total precipitation during the year of sampling and analysis was a little more than 31 inches according to the plot gauges. This amount is somewhat less than the 43-year annual average at Geneva of 33.5 inches, but it would be erroneous to classify the period as a "dry" year. Mid-summer precipitation was considerably greater than ordinarily occurs. This is brought out in Table 2, where comparisons with the average are made on a monthly basis. Other periods of relative wetness or dryness can be ascertained from the table.

However, general weather conditions cannot be tabulated readily. In view of the fact, and because of the importance of weather conditions generally in studies concerned with runoff, a month by month descriptive summary of weather and soil conditions has been prepared to supplement the tabular data. The summary is found in Appendix B.

#### PRESENTATION OF DATA

The results of the analyses of runoff water from individual rains, and other relevant data, are reported in Tables 10 to 17 of Appendix A, as a record of basic data. These tables form the basis of the various condensed tables and graphs that appear throughout the text. An analysis of each separate runoff was necessary before the runoffs could be classified on more than an empirical basis, but discussion in this paper is facilitated generally by such classification. In certain discussions the data on individual rains are required.

Although the analyses covered a period of 13 months, the common use of an annual basis of comparison has made it desirable to confine the discussion chiefly to the data of a 12-month period.

#### TOTAL LOSSES DURING ONE YEAR

The total annual amounts and average concentrations of soluble materials found in runoff water from April, 1938, to March, 1939, appear in Table 3. The results show the magnitude of the annual losses and concentrations which may probably be expected under ordinary conditions at Geneva. Not much greater significance than this can be attached to a summation of data on an annual basis because of the variability in conditions governing runoff that occurs from year to year. While the total amount of precipitation that fell during the period was approximately normal, its distribution was somewhat unusual. Other conditions affecting both the amount and concentration of solutes in runoff are known to vary considerably. The annual totals of Table 3 would have been notably different in some instances if the losses that occurred in March, 1938, had been included instead of those of March, 1939. However, these considerations do not preclude some comment on the annual data.



TABLE 3

LOSSES OF SOLUBLE MATERIALS IN RUNOFF WATER\* DURING THE YEAR APRIL 1, 1938, TO MARCH 31, 1939, FROM GENEVA EROSION PLOTS (ONTARIO LOAM, SLOPE 8 PER CENT; DUNKIRK SILTY CLAY LOAM, SLOPE 5 PER CENT)

	Total Annual Amounts (pounds per acre)									
	Total Solids	Ignited Solids	Loss on Ignition	Nitrogen (total)	Ca	Mg	S	K	Na	Soil Loss
<b>ONTARIO PLOTS</b>										
1. Red clover.....	4.83	2.45	2.39	.48	.45	.08	.15	.16	.18	106.5
2. Rye-fallow.....	33.65	17.58	16.08	.47	4.73	.11	.50	.35	.89	27,623.5
3. Alsike clover.....	5.66	3.12	2.53	.20	.48	.08	.14	.18	.41	247.6
4. Soybeans.....	2.44	1.16	1.28	.20	.14	.06	.05	.05	.12	190.4
5. Fallow.....	50.13	29.12	21.00	.95	5.77	1.33	1.29	.30	1.63	58,848.6
6. Bluegrass.....	1.73	.87	.86	.09	.10	.03	.08	.06	.08	30.5
<b>DUNKIRK PLOTS</b>										
7. Fallow.....	119.37	60.79	58.58	10.39	10.00	2.61	4.15	.82	3.12	99,299.1
8. Corn, 1938.....	137.45	81.88	55.56	9.80	11.98	3.61	5.42	.82	4.71	17,806.3
<b>Average Annual Concentrations (parts per million)</b>										
										Precipitation Lost as Runoff (percentage)
<b>ONTARIO PLOTS</b>										
1. Red clover.....	46.9	23.7	23.2	4.7	4.3	.7	2.1	1.5	1.7	1.5
2. Rye-fallow.....	71.6	37.4	34.2	1.0	9.6	.3	1.1	.8	1.9	6.7
3. Alsike clover.....	43.6	24.1	19.5	1.6	3.9	.6	1.6	1.5	3.4	1.9
4. Soybeans.....	51.7	24.6	27.1	1.1	2.9	1.2	1.5	1.1	2.5	.7
5. Fallow.....	64.3	37.3	26.9	1.3	7.4	1.8	2.0	.4	2.2	11.1
6. Bluegrass.....	13.1	21.8	21.3	2.8	2.5	.7	3.9	1.4	2.0	.6
<b>DUNKIRK PLOTS</b>										
7. Fallow.....	70.1	35.7	34.4	6.1	5.9	1.5	2.9	.5	1.9	24.3
8. Corn, 1938.....	132.9	79.2	53.7	9.5	11.6	3.5	7.4	.8	4.6	14.7

\* All summation data on runoffs are based on only those runoffs in which a given solute was analyzed. Thus sulphur from Plot 2 was determined in only 17 runoffs of 7,150.56 cubic feet per acre, out of the 20 runoffs totaling 7,531.51 cubic feet per acre from that plot during the year.

Maximum losses of solutes occurred in runoff from the Dunkirk plots. The loss of 10 pounds per acre of soluble nitrogen seems most noteworthy from the standpoint of fertility loss, and offers some evidence (to be accepted with reservations) that the relatively low nitrogen losses reported by Duley (11) are not universal. Losses of potassium are less significant, and losses of phosphorus although not reported are known to be negligible, from both the Ontario and the Dunkirk plots. Qualitative tests throughout the experiment either gave negative results or showed traces of phosphorus, but never in amounts to warrant quantitative analysis.

Minimum losses of solutes occurred on the Ontario plots under good cover while intermediate amounts were lost from the fallowed Ontario plots.

The data on annual soil and water losses aid in visualizing the conditions of erosion that accompanied the losses of solutes, and the average annual concentrations may serve as a point of reference to determine whether the concentration of solutes in runoff from individual rains or groups of rains is high or low.

The influence of soil type, vegetation and some other factors may be inferred from the total annual losses and average concentration of solutes lost in runoff water. They can be considered to better advantage later.

#### FACTORS THAT GOVERN SOLUTE LOSSES

Difficulties encountered in attempts to classify the data from the present investigation, were due in part to the fact that the study had been exploratory in nature. Previous investigations have been too brief to provide a critical basis for classification.

Certain difficulties are inherent in the problem. Solute in runoff may be derived from either soil or vegetative cover. Rain water itself contains small amounts of dissolved substances. Translocation of solutes in the soil may be caused by a movement of soil moisture, accompanied by evaporation and solute deposition. The rates of runoff and infiltration obviously affect the amounts of solutes that are moved laterally or downward. In this connection subsurface flow and seepage also must be considered.

Microbial activity and other factors also affect both the relative and absolute concentrations of soluble constituents in the soil or soil solution. Stremme and Schroedter (29) found changes in the soil solution from season to season due to the activities of higher plants and micro-organisms, and from year to year due to varying climatic conditions.

The equilibrium of constituents coming into solution in flowing water or held by the soil because of its properties of absorption or base exchange is not static. It may shift with changing solution concentrations of the various constituents.

Obviously, the effects of all these factors could not be traced in the present investigation. A study of the data gave cumulative evidence as it progressed, however, that relative rates of infiltration and runoff, and surface deposition of soluble materials by capillarity and evaporation, as pointed out by King (17), were of first importance in determining the

TABLE 4

LOSSES OF SOLUBLE MATERIALS IN RUNOFF WATER FROM ONE 4.4 INCH RAIN AUGUST 10, 1938, FROM GENEVA EROSION PLOTS

Total Amounts (pounds per acre)											
Total Solids	Ignited Solids	Loss on Ignition	Nitrogen (total)	Ca	Mg	S	K	Na	Soil Loss	Runoff Water	Density Washoff
										(cu. ft./A)	(lbs./cu. ft.)
ONTARIO PLOTS											
1. Red clover .....	2.04	1.08	.96	.29	.02	.05	.03	.08	88.6	897.33	.10
2. Summer fallow .....	29.26	15.59	13.68	4.25	.04	.34	.30	.81	27,005.5	6,803.82	3.97
3. Alsike clover .....	2.87	1.66	1.21	.38	.02	.07	.08	.15	192.6	1,231.29	.16
4. Soybeans .....	.29	.15	.01	.04	.01	.01	.01	.01	29.9	86.83	.34
5. Fallow .....	27.52	18.38	9.14	4.02	.87	.54	.16	.14	47,864.3	8,712.52	5.49
6. Bluegrass .....	.28	.12	.16	.03	.01	.01	.01	.02	9.6	146.43	.07
DUNKIRK PLOTS											
7. Fallow .....	22.19	11.62	10.57	2.02	.07	.65	.20	.65	91,557.0	10,457.36	8.76
8. Corn .....	12.94	7.81	5.10	1.60	.08	.59	.14	.56	15,589.0	4,489.94	3.47
Concentrations (parts per million)											
											Precipitation lost as runoff (%)
ONTARIO PLOTS											
1. Red clover .....	36.5	19.3	17.2	.4	.3	.9	.6	1.5	..	5.5	...
2. Summer fallow .....	68.9	36.7	32.2	.6	.1	.8	.7	1.9	..	42.0	...
3. Alsike clover .....	37.4	21.6	15.8	.4	.3	.9	1.1	1.9	..	7.6	...
4. Soybeans .....	52.9	26.9	26.0	1.4	.7	1.4	1.1	2.4	..	8	...
5. Fallow .....	50.6	33.8	16.8	.6	1.6	1.0	.3	2.1	..	52.2	...
6. Bluegrass .....	30.8	13.6	17.2	ND	.5	1.1	.8	2.1	..	.9	...
DUNKIRK PLOTS											
7. Fallow .....	34.0	17.8	16.2	1.5	.1	1.0	.3	1.0	..	65.7	...
8. Corn .....	46.2	28.0	18.2	2.4	.3	2.1	.5	2.0	..	28.2	...
Proportion of Annual Loss (percentages, where annual loss = 100%)											
ONTARIO PLOTS											
1. Red clover .....	42.3	44.2	40.3	1.5	21.4	34.7	21.0	46.1	83.2	54.2	...
2. Summer fallow .....	86.9	88.7	85.1	53.7	32.7	68.9	86.6	90.6	97.8	90.3	...
3. Alsike clover .....	50.8	53.1	47.9	21.7	27.8	49.8	46.3	35.7	77.8	59.1	...
4. Soybeans .....	11.8	12.6	11.0	3.8	6.7	15.2	11.5	10.8	15.7	11.1	...
5. Fallow .....	54.9	63.1	43.5	35.8	65.3	42.8	57.1	70.6	81.3	69.7	...
6. Bluegrass .....	16.3	14.2	18.4	ND	16.8	12.8	12.4	24.2	31.5	22.8	...
DUNKIRK PLOTS											
7. Fallow .....	18.6	19.1	18.0	9.1	2.8	14.2	23.0	21.1	92.3	38.2	...
8. Corn .....	9.4	9.6	9.2	6.8	2.0	11.0	16.7	12.0	87.7	27.1	...

concentration of solutes in the initial runoff from each rain. Continued runoff tended to dilute initial concentrations, although the total amount of solutes lost in the runoff was increased. The relationships were sufficiently consistent to justify their use in dividing the annual data into four groups, Tables 4 to 7. The groups are not wholly representative of categories of runoff, but their discussion develops the major principles that govern the concurrent losses of solutes.

The runoff from a single intense summer rain was so distinctive that it is reported separately. Runoffs from eight winter rains and thaws constitute a second group. Runoff from one sudden thaw was so distinctive as to merit a separate class. Most of the runoffs fell into the fourth group of small or medium sized runoffs that occurred chiefly during the summer months.

I. The first group to be discussed is represented only by the runoff from one intense rain of 4.4 inches that fell on August 10. The data are reported in Table 4. This runoff was exceptionally large from the corn and fallow plots and there represents high proportions of the rainfall. Dilution by large quantities of runoff water obscures any concentration of solutes that may have characterized the initial runoff. Consequently the solute concentrations that are reported represent summer minimums<sup>5</sup> and tend to follow the normal solubilities of the two soil types. Ignited solids are higher for the Ontario soil in both amount and concentration.

Variations in the data of the two fallow plots on Ontario soil indicate that winter rye, previously turned under, increased the concentrations but decreased the amounts of solutes lost. The decreased amounts reflect the lower water losses from the plot that carried winter rye.

The Ontario plots under cover absorbed most of the rain that fell. Presumably a marked translocation downward of the solutes in the soil of the covered plots took place, and a correspondingly low concentration of most solutes in runoff was evident. The soybean plot appeared to be exceptional in that the total solids were high for the percentage of rainfall lost as runoff, while the ignited solids were relatively low in comparison with those from the fallow plots. The intermediate position of the soybean plot may be the result of previous crops of soybeans that were incorporated in the soil, that would tend to increase the organic solutes in the soil of this plot. It is equally possible that some excess of organic solute may have been derived directly from the dense soybean cover that occupied the plot at the time this August 10 rain occurred.

There is no evidence of a downward translocation of salts as a result of infiltration on the less permeable Dunkirk plots as the rain progressed, although some undoubtedly took place. The generally lower concentration of solutes in the fallow plot runoff is due in part to dilution by increased runoff, but the relative amounts of runoff indicate that the higher solute concentrations from the corn plot reflect the effect of an alfalfa cover turned under prior to the planting of corn. The latter statement agrees

<sup>5</sup> The high proportions of the annual totals due to this one rain cause these "minimums" to approximate the average annual concentrations.

TABLE 5

LOSSES OF SOLUBLE MATERIALS IN WINTER RUNOFFS 32-39 INCLUSIVE DURING FEBRUARY-MARCH, 1939, FROM GENEVA EROSION PLOTS\*

Total Amounts (pounds per acre)									
Total Solids	Ignited Solids	Loss on Ignition	Nitrogen (total)	Ca	Mg	S	K	Na	Soil Loss
									Runoff Water (cu. ft./A.)
									Density Washoff (lbs./cu. ft.)
<b>ONTARIO PLOTS</b>									
1. Red clover....	1.04	.52	.33	.08	.03	.05	.05	.03	154.25
2. Winter rye....	.68	.30	.09	.04	.04	.04	.02	.01	153.89
3. Alsike clover....	.41	.20	.07	.02	.02	.02	.02	.01	61.27
4. Soybeans, 1938....	.35	.19	.05	.02	.01	.02	.02	.01	82.41
5. Fallow.....	.87	.30	.10	.12	.03	.07	.01	.02	303.01
6. Bluegrass.....	.46	.20	.03	.04	.01	.03	.02	.01	134.98
<b>DUNKIRK PLOTS</b>									
7. Fallow.....	64.34	30.76	7.62	7.10	1.81	3.21	.41	1.61	11,652.51
8. Corn, 1938....	101.22	38.95	7.81	9.60	3.02	4.51	.55	3.61	6,923.61
Average Concentrations (parts per million)									
Precipitation lost as runoff (%)									
<b>ONTARIO PLOTS</b>									
1. Red clover....	108.0	53.7	31.3	8.3	3.1	5.2	5.2	3.1	.7
2. Winter rye....	71.0	30.9	9.4	4.2	4.2	4.2	2.1	1.0	.7
3. Alsike clover....	112.4	53.7	18.3	5.5	5.5	5.5	5.5	2.8	.3
4. Soybeans, 1938....	94.3	43.0	16.2	5.4	2.7	5.1	5.4	2.7	.4
5. Fallow.....	46.0	15.8	5.3	6.3	1.6	3.7	.5	1.1	1.3
6. Bluegrass....	54.1	23.7	3.6	4.7	1.2	3.6	2.4	1.2	.6
<b>DUNKIRK PLOTS</b>									
7. Fallow.....	88.5	42.3	10.5	9.8	2.5	4.4	.6	2.2	49.5
8. Corn, 1938....	234.3	90.2	18.1	22.2	7.0	10.4	1.3	8.4	29.4
Proportion of Annual Loss (percentage, where annual loss = 100%)									
<b>ONTARIO PLOTS</b>									
1. Red clover....	21.5	21.3	68.9	17.8	36.0	31.9	35.0	14.8	9.3
2. Winter rye....	2.0	2.2	18.6	9	28.7	8.3	5.7	1.6	.03
3. Alsike clover....	7.2	6.8	35.4	1.1	23.7	17.3	10.0	2.2	2.0
4. Soybeans, 1938....	14.3	13.7	30.2	16.1	17.2	31.5	31.5	10.2	2.9
5. Fallow.....	1.7	2.0	1.4	2.0	2.2	5.2	2.9	1.1	10.5
6. Bluegrass....	26.3	29.2	31.2	35.1	42.6	41.9	28.1	13.4	2.4
<b>DUNKIRK PLOTS</b>									
7. Fallow.....	53.9	55.2	73.5	71.1	70.0	77.0	49.9	51.5	42.6
8. Corn, 1938....	73.6	76.1	79.9	80.0	84.0	83.0	67.1	76.8	41.8

\* Precipitation January 30 to March 31 was 6.5 inches, of which snowfall was equivalent to 4.6 inches rainfall 1.9 inches.

with statements already made on the turning under of winter rye and soybeans.

II. The late winter runoffs of February and March, 1939, form a second group and are reported in Table 5. The amount of rainfall lost as runoff is low on the Ontario plots and must have resulted in an effective downward movement of solutes so that minimum concentrations could be expected. A tendency in this direction may have been neutralized to some extent by extensive periods of continuously moist conditions that allowed the less soluble components of the soil to come into solution. Low concentrations, however, characterize the runoff from the fallow plot. Its concentration of ignited solids is at nearly the same low level as in the dilute August 10 runoff (Table 4). The winter rye plot formerly summer fallowed shows the same relationship.

The Ontario plots under cover show higher solute concentrations in the winter runoff than do the fallow plots. This, and the relative concentrations shown in Tables 4 and 5, indicate that the winter concentrations reported are due to solutes derived from the weathered vegetation that covered the plots. Leaching of solutes from plants has been reported by LeClerc and Breazeale (22), Guilbert *et al.* (13), and Guyon (14) (15).

The data on the runoffs from Dunkirk soil follow the expected order of solute concentrations, but appear to be relatively too high. The fallow plot runoff is more concentrated than the runoff from the comparable fallow Ontario plot. This is the opposite of what would be expected from the normal solubilities of the two soils and no immediate explanation seems entirely adequate. The fact may be related to the percentages of precipitation lost as runoff, or rather, to the relative permeability of the two soils. Long-continued saturation of the soil, with freezing and thawing, but with little downward movement of solutes on the Dunkirk plots by infiltration, were typical conditions during the winter runoffs. Salts from slowly soluble constituents may have accumulated, and underground seepage from the surrounding alfalfa field may have caused some distortion of the results that were obtained (20).

Thus soil type was clearly the dominant factor influencing these late winter runoffs. The plots on Dunkirk silty clay loam suffered high proportions of their total annual soil, water, and solute losses, while the plots on Ontario loam underwent comparatively small losses.

III. The data of Table 6 on the single thaw runoff of April 12, 1938, offer some contrasts to the data of Table 5. At the time this runoff occurred, weather and soil conditions favored extensive leaching of both surface soil and vegetation, particularly on the more permeable Ontario soil. The resultant runoff from the Ontario plots was correspondingly dilute, but for the fallow Dunkirk plot the comparison with Table 5 shows no appreciable change in solute concentrations as judged by ignited solids. Lack of adequate drainage during the late winter months apparently tends to produce relatively high concentrations of solutes in runoff from Dunkirk soil. The data for Plot 8 are not comparable because of a changed cover on that plot (Table 1).



IV. The data for the large number of remaining runoffs of the year are reported in Table 7. In the main this group is characterized by small and medium sized runoffs, occurring in warm or open weather that is favorable to rapid evaporation of soil moisture. The extended time over which the runoffs occurred involved considerable variation in weather, soil conditions, cultivation, and crop growth. The group accounts for moderate proportions of the annual losses and is characterized in the aggregate by high solute concentrations. Proof of the latter statement is most evident in a comparison of the data of Tables 4 and 7. The high concentrations are attributed in large measure to the removal, in initial runoff, of salts left at the soil surface by capillary rise and subsequent evaporation of soil water, and to the absence of any marked dilution by subsequent runoff.

The effect of one other factor is plainly evident in this group of runoffs. The three plots on which vegetation was turned under (Plots 2, 4, 8) show outstandingly high concentrations of ignited solids and hence of total solids.

Effects that are related to soil type are less evident on first inspection of the data. However, the permeability and texture of the two soils are such that relatively more solutes from surface deposits (induced by capillarity and evaporation) should appear in the Dunkirk runoffs. That this was the case is shown by the following considerations:

Total and ignited solids from the two permanently fallow plots on the two soils are nearly identical. This is in marked contrast to the data of Table 4, where the comparable concentrations were approximately twice as great in the Ontario runoff. To be consistent, the relatively greater increase of solutes in the Dunkirk summer runoffs of smaller volume must be attributed to greater surface salt concentrations on that soil. The effect undoubtedly would have been greater if the amounts of water lost from the fallow plots were more nearly identical. The more impermeable Dunkirk soil lost less water than did the Ontario soil in the small or medium sized runoffs under discussion, and therefore suffered a greater downward movement of accumulated surface salts. The inversion of the expected order was due apparently to damming by clods and other surface irregularities on the Dunkirk plot. The Ontario fallow generally presented the smoother surface because of the manner in which the two soils responded to cultivation.

Some, but not all, of the miscellaneous factors that appreciably affect small runoffs can be illustrated from the basic data for individual runoffs that are given in the Appendix. Cultivation, mentioned above, tends to increase infiltration during the first succeeding rain at least, and to prevent the surface deposition of salts by capillarity and evaporation. Under such conditions, runoff water tends to be of low solute concentration as is shown for the Dunkirk plots by the June second runoff that followed cultivation on May 31 (Tables 16 and 17).

A high moisture content in the soil at the beginning of a rain tends to lower initial infiltration. This may result in high solute concentrations if



TABLE 7

LOSSES OF SOLUBLE MATERIALS IN ALL MEDIUM-SIZED TO SMALL RUNOFFS FROM GENEVA EROSION PLOTS DURING ONE YEAR APRIL, 1938, TO MARCH, 1939, EXCEPTING ONLY THE ABNORMAL RUNOFFS OF APRIL 12, AUGUST 10, AND FEBRUARY-MARCH (SUMMARY OF RUNOFFS 4, 6-21, 23-31, FROM PRECIPITATION OF 17.3 INCHES)

Amounts (pounds per acre)											
Total Solids	Ignited Solids	Loss on Ignition	Nitrogen (total)	Ca	Mg	S	K	Na	Soil Loss	Runoff Water	Density Washoff
										(cu. ft./A.)	(lbs./cu. ft.)
ONTARIO PLOTS											
1. Red clover....	1.09	.54	.10	.05	.03	.05	.06	.04	13.1	113.81	.11
2. Rye-fallow....	3.16	1.81	.10	.23	.05	.12	.02	.05	609.7	205.21	2.97
3. Alsike clover....	1.61	.93	.04	.06	.03	.05	.06	.05	52.5	250.21	.21
4. Soybeans.....	.99	.51	.06	.05	.04	.03	.02	.06	153.6	53.12	2.89
5. Fallow.....	21.09	9.78	.48	1.60	.43	.68	.12	.42	10,960.9	2,710.08	4.04
6. Bluegrass.....	.58	.32	.05	.03	.01	.04	.03	.02	20.9	57.35	.36
DUNKIRK PLOTS											
7. Fallow.....	8.04	4.36	.50	.66	.18	.29	.09	.19	3,239.1	1,037.17	3.12
8. Corn, 1938.....	8.53	3.85	.45	.65	.17	.32	.09	.19	1,399.5	672.11	1.95
Average Concentrations (parts per million)											
Precipitation lost as runoff (%)											
ONTARIO PLOTS											
1. Red clover....	156.3	78.1	13.4	7.8	3.9	8.2	8.9	6.1	...	.2	...
2. Rye-fallow....	246.8	105.4	8.2	18.0	5.6	9.7	2.0	4.3	...	.3	...
3. Alsike clover....	104.8	59.6	3.7	8.7	4.6	8.5	9.1	8.6	...	.4	...
4. Soybeans.....	336.2	173.2	20.5	15.9	14.7	12.9	7.3	21.6	...	.1	...
5. Fallow.....	124.7	57.8	3.1	9.5	3.0	6.4	.9	2.9	...	4.3	...
6. Bluegrass.....	161.5	89.8	13.5	7.1	2.7	12.1	8.5	4.5	...	.1	...
DUNKIRK PLOTS											
7. Fallow.....	124.1	56.8	7.9	10.2	3.1	6.5	1.7	3.6	...	1.7	...
8. Corn, 1938.....	203.3	111.6	11.1	15.9	4.5	8.1	4.1	8.6	...	1.1	...
Proportion of Annual Loss (percentage, where annual loss = 100%)											
ONTARIO PLOTS											
1. Red clover....	22.5	22.8	19.7	12.1	36.2	33.4	39.9	23.7	12.3	6.9	...
2. Rye-fallow....	9.4	11.3	20.9	5.1	35.9	22.8	6.6	5.7	2.2	2.7	...
3. Alsike clover....	28.9	27.9	20.6	12.1	40.9	32.8	33.7	11.2	21.2	12.0	...
4. Soybeans.....	40.7	37.7	32.8	34.6	65.5	53.3	40.0	53.4	80.7	6.8	...
5. Fallow.....	42.1	33.6	49.5	27.7	32.2	52.0	38.0	25.7	18.6	21.7	...
6. Bluegrass.....	33.4	36.8	58.3	25.0	33.8	45.3	53.2	20.5	68.5	8.9	...
DUNKIRK PLOTS											
7. Fallow.....	6.7	7.4	4.8	6.6	7.0	6.8	10.1	6.0	3.3	3.8	...
8. Corn, 1938.....	6.2	5.7	4.6	5.4	4.8	6.0	11.2	4.2	7.4	4.1	...

the weather preceding the rain has favored rapid evaporation and a corresponding rise in soluble salts. On the other hand, it may result in low salt concentrations in runoff water if little or no evaporation has followed previous precipitation. Both cases are illustrated in Tables 11 and 14 by the data on ignited solids in the runoffs from Plots 2 and 5 that followed successive rains on June 11 and 12. Previous rain had occurred on June 7.

Increasing length of time between rains intensifies the drying out of the soil even though rate of evaporation may be low. The first runoff after a long rainless period may therefore carry high concentration of soluble salts, although obviously, the relative rates of infiltration and runoff may mask this effect. The runoffs of November 19 from the Dunkirk plots, and of January 2 or 5 from all the plots, were the first after a long rainless period and carried high solute concentrations.

Conditions of cover changed during the year more on soybean Plot 4 than on any other plot. Consideration of total losses on this plot should take into account the stage of growth reached by the crop. On July 14, when the plot had only a young and ineffective cover, its losses of water and solute concentrations were of the same order as those from the Ontario fallow plot. In contrast, the soybean cover had become so dense by August 10 that losses of soil, water, and solutes were kept to figures almost as low as those from the bluegrass plot.

#### RELATIONSHIPS OF SOIL, WATER, AND SOLUTE LOSSES

The proportion of soil to water in the runoff from the plots does not appear to have any marked effect on the concentration of solutes in runoff, and by inference has no marked influence on the amount of solutes lost. Surface vegetation and the entire soil surface contribute to the amount of solutes carried away. In Table 3 for total annual losses, fallowed Dunkirk Plot 7 shows a washoff density about three times as great as that of Dunkirk corn Plot 8, yet it shows a concentration of ignited solids of only half as much. The Ontario fallow plots show higher washoff densities and higher concentrations than do the Ontario plots under cover, but the corresponding relationship is not evident when only the two fallow plots are compared. It can be shown that many individual runoffs of high solute concentration carried but little soil.

The effects of soil and water losses, separately, on solute losses, can best be shown by considering the proportions of the total annual amounts of each that occurred in each group or runoffs, Tables 4 to 7. If perfect correlation existed among the three kinds, their proportional losses in each group would be identical. A glance through the tables is sufficient to show that this is far from the case.

The lack of any dependable relationship between soil and solute losses is most evident in Table 6. Although no soil was lost from any of the Ontario plots by this single thaw runoff, losses of ignited solids on these plots amounted to as much as 29.6 per cent of the annual total. The Dunkirk fallow Plot 7 lost nearly 20 per cent of the annual total of

ignited solids and only 1 per cent of the annual total of soil. Similar lack of correlation is evident throughout the tables.

The data also fail to show any dependable relationship between water and solute losses. Since runoff water is the direct agent of solute removal some relationship should be evident, however, if other factors are inactive or are eliminated. To a degree this situation characterizes the August 10 runoff from the Ontario plots, Table 4. The plots lost solute and water in the same order and in proportionate amounts. The same trend is evident in Table 6, but is less evident in Table 5, and is obscure in Table 7, for causes that have been stated previously.

#### THE EFFECT OF FERTILIZATION

Fertilization of the plots during the investigation included the turning under of green manure or crop residues and the application of commercial 5-10-5 fertilizer. Earlier discussion has covered the general effects of turning under vegetation on solute losses. A noticeable increase in concentration of solutes, especially volatile solids, usually followed such treatment.

Results arising from the application of commercial fertilizer are not discernible in the grouped data that have been discussed, nor are they plainly evident elsewhere. However, the basic data on individual runoffs, available in the Appendix, show some variation that is due, apparently, to the commercial fertilizer that was applied to the plots.

An application of fertilizer was made in early June to the Ontario Plots 2, 4, and 5, at the rate of 500 pounds per acre. It caused (30) or at least certainly preceded an increase in the concentration of solutes relative to the amount of runoff water from these plots. The relatively high concentrations of the June-July runoffs is in contrast to both the earlier April-May runoffs and the later summer and fall runoffs from the same plots.

The Dunkirk plots also show some effects that are attributable to fertilization. Their runoffs are grouped on a seasonal and cultural basis in Table 8 for amounts and concentrations of ignited solids, calcium, and nitrogen.

The major variables between these plots were fertilization and plant cover, both present on Plot 8, but absent from Plot 7. Alfalfa sod on Plot 8 was spaded under April 27, and corn was planted in June.

Immediately after fertilization of Plot 8 on June 9, and for most of the rest of the year, solute concentrations in runoff water from that plot increased, and remained at a fairly consistent higher level than those from the unfertilized fallow plot. They had, however, already increased somewhat in the May 16-June 7 runoffs after the alfalfa sod had been spaded under. Noticeable fertilizer effects on Plot 8 seemed to fade out during the fall runoffs when the maturing corn caused a marked restriction in runoff volume. Decreased concentrations in the fall runoffs may therefore have been due in part to increased infiltration.

TABLE 8

SEASONAL VARIATIONS IN LOSSES OF SOIL AND WATER, AND IN AMOUNTS AND CONCENTRATIONS OF IGNITED SOLIDS, CALCIUM, AND TOTAL NITROGEN FROM CORN PLOT 8 (FOLLOWING ALFALFA SOD) AND CONTINUOUS FALLOW PLOT 7 ON DUNKIRK SILTY CLAY LOAM

RUNOFFS						
Dates	Number Analyzed		SOIL LOSS in Pounds per Acre		WATER LOSS in Cu. Ft. per Acre	
	Plot 8	Plot 7	Plot 8	Plot 7	Plot 8	Plot 7
Mar. 2-Apr. 22. . . . .	7	7	397	2,745	8,520.5	7,143.7
May 16-June 7. . . . .	4	4	396	432	56.2	70.6
June 11-July 28. . . . .	8	8	627	1,353	150.6	306.6
August 10. . . . .	1	1	15,589	91,557	4,489.9	10,457.4
Aug. 30-Sept. 22. . . . .	5	6	107	315	43.1	176.0
November 19 . . . . .	1	1	0.1	0.5	5.6	9.1
January 2, 5. . . . .	2	2	0	6	113.8	177.4
Feb. 13-Mar. 30. . . . .	8	8	768	3,488	6,923.6	11,652.5
			Total Amounts in Pounds per Acre		Average Concentra- tions in Parts per Million	
			Ignited Solids			
Mar. 2-Apr. 22. . . . .	7	7	12.16	16.80	22.9	37.7
May 16-June 7. . . . .	4	4	.34	.33	97.8	75.7
June 11-July 28. . . . .	8	8	2.28	1.38	242.8	72.4
August 10. . . . .	1	1	7.84	11.62	28.0	17.8
Aug. 30-Sept. 22. . . . .	5	6	.26	.34	47.4	30.6
November 19. . . . .	1	1	.06	.10	164.3	175.7
January 2, 5. . . . .	2	2	.56	.67	78.9	60.8
Feb. 13-Mar. 30. . . . .	8	8	62.28	33.58	144.2	46.2
			Calcium			
Mar. 2-April 22. . . . .	7	7	1.13	1.06	2.1	2.4
May 16-June 7. . . . .	3	4	.07	.06	25.1	14.8
June 11-July 28. . . . .	8	8	.45	.34	47.6	18.0
August 10. . . . .	1	1	1.60	2.02	5.7	3.1
Aug. 30-Sept. 22. . . . .	5	6	.05	.09	19.1	8.0
November 19 . . . . .	1	1	.01	.01	15.6	9.5
January 2, 5. . . . .	2	2	.07	.11	9.4	10.2
Feb. 13-Mar. 30. . . . .	8	8	9.60	7.12	22.2	9.8
			Total Nitrogen			
Mar. 2-Apr. 22. . . . .	5	4	.97	1.39	3.2	4.9
May 16-June 7. . . . .	4	4	.04	.04	11.9	8.5
June 11-July 28. . . . .	7	8	.16	.21	20.7	11.0
August 10. . . . .	1	1	.66	.95	2.4	1.5
Aug. 30-Sept. 22. . . . .	4	6	.04	.07	15.5	6.2
November 19. . . . .	1	1	.02	.05	65.9	88.4
January 2, 5. . . . .	2	2	.07	.06	10.1	5.9
Feb. 13-Mar. 30. . . . .	8	8	7.81	7.61	18.1	10.5

The concentrations of solutes from the Dunkirk plots in the large February–March, 1939, runoffs are not subject to wholly logical explanation, but may have been affected by subsurface seepage from the surrounding alfalfa field (20).

The decrease in the effect of fertilizer on runoff composition with increasing length of time after application, as observed by Keiller (16), was essentially the trend observed in the present investigation. The generally small amount of solute loss clearly attributable to fertilizer also agrees with Keiller's conclusion that little loss of a soluble fertilizer occurs in runoff unless runoff is very rapid.

#### LOSSES OF SPECIFIC CONSTITUENTS

In the previous discussion of runoff water solutes, most attention has been given to the determinations of total or ignited solids with but brief reference to the specific constituents that were included therein. This was necessary for simplification; it was also justified by the fact that in many cases the amounts of the specific constituents were too small to present differences that were reliable or significant. There are certain points in connection with the specific constituents, however, to which attention should be directed.

It may also be pointed out that sulphur and the metallic constituents do not wholly account for the total ignited solids that have been reported. Separations made during the analyses showed that the ignited solids contained appreciable amounts of silica and the oxides of iron and aluminum. However, quantitative estimations of the amounts of these constituents were not made.

Several statements may be made with respect to nitrogen. The data of Table 3 may overemphasize the difference in soil type with respect to this element, since the annual nitrogen losses from the Dunkirk plots averaged about twenty times as much as the nitrogen losses from the Ontario plots. Losses of nitrogen from the Dunkirk plots tended to be higher throughout the year, but even so did not exceed the Ontario losses by more than 10 pounds per acre. The disparity that does exist is due principally to the effect of runoffs during February and March, 1939, (Table 5), when the excess of nitrogen loss from the Dunkirk plots was about 7.5 pounds per acre. Throughout the greater part of the year the difference in nitrogen losses between soil types is not so strikingly pronounced.

Nitrates apparently did not constitute a large part of the total nitrogen of the runoff water. This was indicated by qualitative nitrate tests made frequently throughout the investigation. Duley (11) found that the greater part of the nitrogen in runoff water is in some organic form. This is in marked contrast to drainage waters from lysimeters wherein the nitrogen is almost wholly in the form of nitrates (2) (19) and to rain water which brings down nitrogen mostly as ammonia but partly as nitrates or organic nitrogen (7).

Collison and Mensching (7) found the mean yearly addition of

nitrogen in rainfall to be 8.93 pounds per acre at Geneva over the period 1918-28. The mean concentration of nitrogen in rainfall was 1.13 parts per million, and the nitrogen was well distributed throughout the year. In the present study the Dunkirk plots lost more than that amount and several times that concentration of nitrogen in runoff. The Ontario plots, however, all lost much less nitrogen in runoff than Collison found in rainfall.

In general, calcium was lost in greater amounts than any other specific constituent that was determined. For this reason calcium losses follow closely the order of ignited solids, and arguments that have been based on the latter determination could have been based equally well on the former.

Maximum losses of calcium did not occur at the same time from the Ontario and from the Dunkirk soils; wide variability in the concentrations of solutes in different runoffs has already been indicated. Maximum losses of calcium from the Dunkirk plots occurred during the February and March runoffs of 1939. The fallow and rye fallow were the only Ontario plots to lose as much as four or five pounds of calcium per acre per year. The major portion of the calcium losses from these plots occurred during the large runoff of August 10.

Expression of the variability of runoff composition is clarified somewhat by the data of Table 9, where the relative proportions of calcium, of nitrogen, and of the sum of magnesium, sulphur, potassium, and sodium are reported for the two groups of runoffs just mentioned. These data show that both the Dunkirk and the Ontario soils lost more calcium proportionally in the August 10 runoff than in the winter runoffs. The composition of the Ontario runoff is more variable than that of the Dunkirk runoff, with respect both to nitrogen and to the sum of magnesium, sulphur, potassium and sodium. Similar ratios for the

TABLE 9

PROPORTIONS OF CALCIUM TO TOTAL NITROGEN, AND TO THE SUM OF MAGNESIUM, SULPHUR, POTASSIUM, AND SODIUM IN 3 GROUPS OF RUNOFFS, IN WHICH THE AMOUNT OF CALCIUM IS ARBITRARILY PLACED AT A BASE OF 10

	August 10 runoff (Table 4)		February-March runoffs (Table 5)		Medium-sized to small runoffs (Table 7)	
	Ca : N	Ca : sum	Ca : N	Ca : sum	Ca : N	Ca : sum
ONTARIO PLOTS						
1. Red clover.....	10 : .7	10 : 6.3	10 : 11.8	10 : 19.6	10 : 17.6	10 : 33.7
2. Rye-fallow.....	.6	3.6	21.8	29.2	4.3	10.5
3. Alsike clover.....	1.2	8.6	36.8	35.5	7.3	32.0
4. Soybeans.....	1.9	7.8	27.3	25.1	13.8	31.8
5. Fallow.....	.9	6.9	8.8	10.9	3.0	10.4
6. Bluegrass.....	ND	14.4	7.7	20.3	19.1	36.6
DUNKIRK PLOTS						
7. Fallow.....	4.7	7.9	10.7	9.9	7.5	11.2
8. Corn, 1938.....	4.2	8.6	8.1	12.2	6.9	12.0

medium and small runoffs of the year appear also in Table 9. They emphasize the relatively high winter losses of nitrogen as compared to other constituents.

Observations made during the investigation and an over-all consideration of the data have led to some further conclusions regarding specific constituents.

Magnesium appeared to be less mobile than calcium, and showed a proportionately smaller increase in the runoffs where previous conditions had favored evaporation and salt rise. The few exceptional runoffs in which magnesium either exceeded or was about equal to calcium all occurred during cool seasons of the year. They were mostly cases of disproportionately low calcium rather than of disproportionately high magnesium.

Sulphur in runoff water did not appear to be diminished as much by good plant cover as was calcium. Soybeans and bluegrass both allowed about 150 per cent as great an average concentration of sulphur as of calcium in runoff, while clover sods permitted only about 50 per cent. The corresponding percentage for the Ontario fallow and rye fallow plot were 26 per cent and 12 per cent, respectively. Thus there was some tendency for total losses of sulphur to parallel those of nitrogen from the various plots, possibly reflecting the similar occurrence of the two elements in rainfall and organic materials.

Ratios of sulphur to calcium vary considerably and are generally lower than the stoichiometric ratio of the two elements in calcium sulphate, although probably the major portion of the sulphur was lost in sulphate form. Calcium in runoff water probably occurred more often in combination with carbonates or bicarbonates than with sulphates, particularly in summer runoffs when capillarity and upward movement of soil salts were most effective in increasing runoff solutes. Marked effervescence<sup>6</sup> often occurred during the analytical procedure when a few drops of dilute hydrochloric acid were added to the evaporated runoff residues. Collison (5) found that in leachate from Ontario loam soil in the Geneva lysimeters "by far the largest amount of the bases was lost as bicarbonate, about  $\frac{1}{5}$  to  $\frac{1}{2}$  of that amount as sulphate and only  $\frac{1}{6}$  to  $\frac{1}{5}$  as much as chloride."

Losses of potassium and sodium were less than the losses of other specific constituents, and are therefore subject to greater relative error. It may be noted, however, that plant cover appeared to affect potassium losses. While the fallow plots lost the greater actual amounts of this element the plots under good cover lost the higher concentrations, thus indicating that part of the loss was derived from vegetation.

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<sup>6</sup> Such effervescence from bicarbonates was observed to be most marked in the late winter runoff water samples from the Dunkirk plots. This fact fits in with Kohnke's observation (20) that the concentration of bicarbonate ion in runoff water generally increases with the proportion of ground water. The observed late winter seepage from the surrounding alfalfa field was thus assumed to be a factor in causing the high solute concentrations then found in the runoff from the Dunkirk plots.

## ADDITIONAL EVIDENCE ON THE TRANSLOCATION OF SOLUBLE SALTS

Circumstantial evidence had indicated early in the investigation that salt concentrations at the soil surface due to capillarity and evaporation were noticeably affecting the concentration of solutes in runoff. The evidence included the fact that Dunkirk runoffs were often more concentrated, other factors considered, than were the Ontario runoffs. The physical characteristics of the two soils are such that a greater effect from salt translocation on the Dunkirk soil could be postulated.

More direct evidence of unusual salt concentrations at the soil

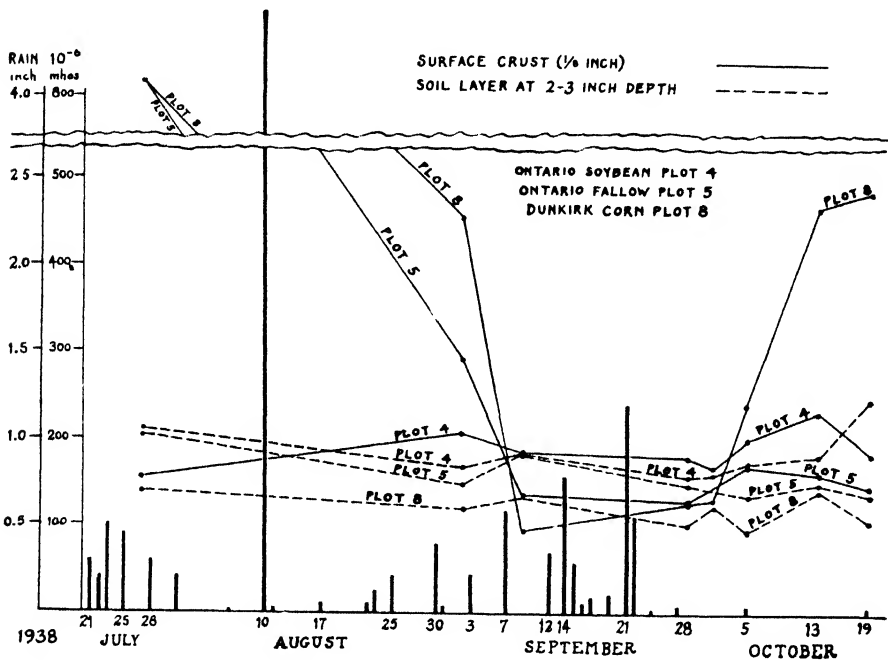


FIG. 1. Conductivity measurements of soil samples from certain plots as an indication of evaporation and salt rise in relation to rainfall during summer and fall, 1938.

surface was obtained from a number of conductivity determinations (9) that were made on the soils at various times. The data that were taken during the summer of 1938 for some of the plots appear in Figure 1. The occurrence of rainfall is also recorded.

Conductivities and salt concentrations are frequently higher in the surface  $\frac{1}{8}$  inch crust than they are in the 2- to 3-inch layer of the fallow and corn plots. Evaporation was undoubtedly high at times from these plots. The soybean plot shows consistently low salt concentrations in both layers, with minor variations. This plot carried a dense cover; consequently water was lost by transpiration rather than by evaporation, and increases of salts at the soil surface were small.



The marked changes in conductivity shown in Figure 1 are undoubtedly associated with changes in general weather conditions. The high conductivities of the surface crusts of the corn and fallow plots on July 27 reflect the effect of two days of hot drying weather that followed the rains of July 21 to 25, during which time the soil had been thoroughly wetted. Conditions were therefore favorable to a maximum rise of salts in a limited time. The unusually high conductivities were duly reflected in the chemical analyses of the runoffs from a shower of high initial intensity that occurred on July 28.

Similar conditions prevailed as to the nature of weather conditions and the length of time since the last previous rain, at the next sampling, September 2. Plots 5 and 8 both had high salt concentrations in the surface crust, although not as high as on July 27. No confirmatory check of this sampling by the analyses of the next runoff, September 7, was possible, because a light rain of mild intensity that caused no runoff had fallen on September 3, and presumably had dispersed the surface salts downward through the upper few inches of soil. Conditions favorable for minimum evaporation prevailed during the intervening period.

The September 8 conductivities reflect the predominant leaching effect of the rain of the day before in that they were even lower at the surface  $\frac{1}{8}$  inch than they were in the 2- to 3-inch layer of both Plots 5 and 8.

The dry period of late September caused no apparent concentration in the surface crusts of Plots 5 and 8. This may have been due to the prevailing cool weather and a lowered rate of evaporation. On October 5 the Plot 8 samples showed some surface salt concentration.

The cool period ended October 9 and a period of unseasonably warm weather followed, with no rain prior to the samplings that were made on October 13 and 19. The conditions favorable to evaporation and salt rise were duly reflected in the high conductivity of the Plot 8 surface sample, but failed to appear for Plot 5. This divergence in plot behavior, contrasting to the close agreement that was shown earlier in the season, is probably associated with soil type differences. Presumably the coarser texture and less compact structure of the Ontario loam soil did not support a consistent capillary rise of water and salts under the only moderately favorable evaporation conditions of late fall.

During the summer of 1939, additional samples were taken on these and other plots for conductivity measurements. The data are not reported, but they gave additional evidence to substantiate the trends that appeared in the data for 1938.

#### LYSIMETER INVESTIGATIONS AS RELATED TO RUNOFF WATER ANALYSES

Solute losses in the runoffs of the present investigation have been considered relatively small. A study of the factors that cause variability in losses of solutes in runoff indicates that under certain conditions greater losses may be incurred, but these conditions were not met at Geneva.

Both runoff and drainage water act to remove soluble salts, and

lysimeter investigations on this action have been carried out rather extensively. The importance of the losses that were incurred in runoff can be judged to some degree by the results of lysimeter studies that have been made on soils similar to those of the Geneva plots.

Collison (5) (6) has made a study at Geneva of solute losses in leachate, using lysimeters filled with a heavy phase of Ontario loam soil. Lyon and Bizzell (2) (23) carried out a similar study with Dunkirk silty clay loam at Ithaca. Data from these investigations have been compared with the results from our runoff studies. It is evident that the drainage water from the lysimeter was not only much greater in amount than was runoff water from similar soils of the erosion plots, but carried generally much greater concentrations of solutes. Extensive limitations must be applied, however, in making the comparison.

No attempt was made with lysimeters to evaluate the effects of variable amounts of rainfall or leachate; no runoff could occur. The filled-in soils of these lysimeters were probably altered from a natural field soil to such a degree as to bring into question the validity of an application of lysimeter data to runoff water studies even on the same soil type. Comparisons between planted lysimeter soils and erosion plot soils involve questionable assumptions as to similarity of plant cover. The lysimeter soils were all quite heavily fertilized throughout the periods of investigation, while only four of the eight erosion plots were fertilized.

In view of these limitations it should be obvious that the comparison is made solely to arouse speculation in regard to the relative solute losses by runoff and by leaching. There are several points, however, which apply to any consideration of the relative effectiveness of runoff water and drainage water as competing agents of soluble salt removal from the soil.

Most lysimeter drainage at both Geneva and Ithaca occurs during the winter or early spring months when the soil is saturated throughout. Runoff occurs not only then but also to a great extent throughout the summer season, when the concentrations of solutes it carries may be greatly increased by a surface deposition of salts as the result of capillarity and evaporation.

There is no reason to assume that the water saved from loss by runoff would necessarily be lost in drainage, since during the summer months the water utilization capacities of evaporation and transpiration are seldom satisfied.

Soil-derived solutes in runoff are removed solely from the surface soil unless subsurface seepage is involved. Drainage water passes through the subsoil before it escapes. Runoff water therefore tends to approach a solution equilibrium with the surface soil, while drainage water tends to approach a solution equilibrium with the subsoil or, more specifically, with the last soil zone through which it has passed (20).

#### GENERAL CONCLUSIONS

The amounts of soluble material that were lost in runoff and a consideration of the factors that affect such losses indicate that the removal

of solutes in runoff water does not constitute an important factor in soil depletion,<sup>7</sup> or in the loss of applied fertilizers,<sup>8</sup> under most circumstances.

It is reasonable to assume that solute losses much higher than those reported here are occasionally incurred during flash runoffs from relatively impermeable soils. A series of such runoffs with intermittent periods favorable to evaporation and the rise of soluble salts would in due time remove large quantities of soluble materials. Good cover would tend to reduce these losses, and maximum solute losses would generally be associated with fallow soils, when the losses of actual soil would also be large. Thus any depletion of the soil due to losses of solutes in runoff is almost invariably rendered relatively inconsiderable by the magnitude of the accompanying soil losses.

There are some possible exceptions. On soils already depleted, low infiltration rates and poor cover undoubtedly hasten the rate at which further exhaustion of the soil takes place. At low nutrient levels solute losses in runoff water may be sufficient to continue the depletion of idle or abandoned land even though a sparse cover and an erosion pavement prevent any major soil losses. On such lands, beneficial effects may follow contour furrowing not only because of the interception and conservation of runoff water, but also because of the retention of the soluble nutrients dissolved in it. The conservation of traces of soluble nitrogen produced slowly by any mode of fixation or supplied by rain water may well govern the succession of growths that ultimately result in a climax vegetation.

Solutes in runoff water may be carried entirely off the fields into streams or they may be reabsorbed on lower-lying soil to contribute to the fertility of that soil at the expense of soil on the slope. In the latter case such transported solutes, from the standpoint of a long-time cumulative effect, may possibly rank in importance with the intercepted runoff water and top soil in causing the high fertility level of many bottom soils and of the small local accumulations along the lower edge of hills and sloping fields. It is not assumed, however, that the reabsorption of runoff solutes is invariably beneficial. The unfavorable conditions that result in regions of low rainfall from cumulative increments of water borne sodium are well known.

#### SUMMARY

Filtered runoff water from eight .01 acre plots, representative of two soil types and seven kinds of cover, has been analyzed for materials in solution. In all, thirty-nine separate runoffs that occurred over a 13-month period have been analyzed.

Small amounts of soluble materials were lost in runoff water.

<sup>7</sup> Duley (11) reported losses from the Columbia, Missouri, plots that are several times as great as the Geneva, New York, losses. His are the only data based on runoff water analyses that appear to be available for direct comparison by season and year.

<sup>8</sup> Surface applications of fertilizer are subject to appreciable washing. Rogers (27) reports losses of as much as 13 per cent of applied superphosphate. The relative amounts removed mechanically and in solution, are not stated.

Soil type and cover had a marked effect on both the amounts and concentrations of the solutes lost in runoff. Their effects appeared to be related to variations in solute concentrations at the soil surface and to the relative rates of infiltration and runoff.

Concentrations of solutes in runoff appeared to be increased by the salts brought to the soil surface by capillarity and evaporation. Conversely, the concentration of solutes in runoff appeared to be decreased by the downward movement of solutes that accompanied infiltration.

Because of the vertical movements of soil salts, flash runoffs that followed conditions favorable to capillarity and evaporation were highest in solution concentration. Additional runoff tended to dilute initial runoff and so lower the concentration of solutes, although the total amounts lost were necessarily increased.

The concentration of solutes is normally greater in the Ontario than in the Dunkirk soil, but the vertical movement of soluble salts, and the greater impermeability of the latter soil, were apparently adequate to produce solute losses in runoff in an inverse order to the normal concentrations in the soil solution.

The amounts and concentrations of solutes in runoff could not be characterized sharply on a seasonal basis, although concentrations tended to be higher in the summer months when evaporation was most effective.

Solutes in some runoffs appeared to be derived in part from the leaching of vegetation.

The amount of soil carried in runoff had no major effect on the concentration of solutes in runoff.

The proportional losses of the separate soluble constituents in runoff varied considerably. No particular analysis can be considered as representative of the runoff from even a single soil type.

Applied fertilizers only temporarily increased the losses of solutes.

Turning under alfalfa sod presumably aided in increasing the concentration of solutes but in decreasing the amount of runoff, on Dunkirk soil. Turning under winter rye on Ontario soil decreased both the concentration of solutes and the amount of runoff. Infiltration and therefore leaching were probably greater in the Ontario soil than in the Dunkirk soil.

Although losses of solutes reported in runoff are small, an analysis of the factors that produce variability in runoff losses indicates that appreciable losses may be incurred under less favorable conditions.

Attention has been called to the similarities and dissimilarities of solute losses in runoff and in drainage water.

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**APPENDIX A**  
**TABLES OF BASIC DATA**



TABLE 10

BASIC DATA FOR ONTARIO RED CLOVER SOIL PLOT 1: LOSSES OF SOIL AND WATER AND CONCENTRATIONS OF SOLUBLE CONSTITUENTS IN THE WATER OF 15 RUNOFFS DURING A 13-MONTH PERIOD 1938-39, WITH TOTAL LOSSES AND AVERAGE CONCENTRATIONS FOR 12 RUNOFFS DURING ONE YEAR APRIL 1, 1938, TO MARCH 31, 1939

Runoff		Soil loss (lbs./A)	Density washoff (lbs. soil /cu. ft.)	Total solids (ppm)	Ignited solids (ppm)	Loss on Ignition (ppm)	Total N (ppm)	Ca (ppm)	Mg (ppm)	S (ppm)	K (ppm)	Na (ppm)
No.	Date											
1	Mar. 2	67.30	.01	62.0	28.6	33.4	ND	4.4	ND	ND	ND	ND
2	Mar. 5	14.96	.01	54.6	33.2	21.4	ND	4.2	.6	ND	.0	3.0
3	Mar. 23	15.17	.10	129.1	82.8	46.3	3.0	1.3	.9	ND	1.5	1.7
4	April 1	5.81	.26	339.0	101.7	237.3	72.5	3.4	3.6	ND	21.0	6.6
5	April 12	490.38	.0	21.7	9.8	11.9	1.1	.7	.2	ND	.2	.9
8	May 16	6.03	.02	154.6	103.1	51.5	18.9	4.3	2.4	ND	5.2	5.7
17	July 14	2.42	3.07	ND	ND	ND	9.8	ND	ND	ND	ND	ND
22	Aug. 10	897.33	.10	36.5	19.3	17.2	.4	5.2	.3	.9	.6	1.5
26	Sept. 14	6.20	.66	157.5	88.2	69.3	18.0	17.5	5.8	8.8	9.6	5.6
30	Jan. 2	36.86	.	253.2	117.8	135.4	21.1	6.5	5.4	13.1	16.9	10.3
31	Jan. 5	53.49	.	77.2	47.8	29.4	1.4	8.7	3.1	5.2	2.9	3.4
33	Feb. 20	40.06	.	138.9	60.5	78.1	28.9	4.7	2.3	7.9	7.5	3.4
34	Feb. 26	5.47	.	339.6	127.9	211.7	213.4	5.0	3.6	14.2	43.2	2.4
35	Feb. 28	78.53	.	66.1	27.6	38.5	34.6	4.2	1.5	2.7	3.5	1.5
39	Mar. 30	30.19	.16	133.9	101.9	32.0	4.3	24.2	6.6	5.8	1.9	5.3
1 year		1,654.77	.06	46.9	23.7	23.2	4.7	4.3	.7	2.1	1.5	1.7

TABLE 11

BASIC DATA FOR ONTARIO SUMMER FALLOW.—WINTER RYE PLOT 2: LOSSES OF SOIL AND WATER AND CONCENTRATIONS OF SOLUBLE CONSTITUENTS IN THE WATER OF 23 RUNOFFS DURING A 13-MONTH PERIOD 1938-1939, WITH TOTAL LOSSES AND AVERAGE CONCENTRATIONS FOR 20 RUNOFFS DURING ONE YEAR APRIL 1, 1938, TO MARCH 31, 1939

Runoff		Soil loss (lbs./A)	Density washoff (lbs. soil /cu. ft.)	Total solids (ppm)	Ignited solids (ppm)	Loss on ignition (ppm)	Total N (ppm)	Ca (ppm)	Mg (ppm)	S (ppm)	K (ppm)	Na (ppm)
No.	Date											
1	Mar. 2	60.89	.01	65.4	34.0	31.4	ND	3.1	ND	ND	ND	ND
2	Mar. 5	32.05	.01	49.3	26.9	22.4	ND	3.1	ND	ND	.3	2.2
3	Mar. 23	10.32	2.91	146.4	109.3	37.1	1.4	5.2	3.7	ND	1.6	3.3
4	April 1	6.30	2.13	127.6	91.4	36.2	2.3	5.7	4.1	ND	1.2	2.8
5	April 12	368.59	..	23.9	11.1	12.8	1.4	.7	.2	ND	.2	.8
8	May 16	6.06	.13	251.9	181.4	70.5	17.9	13.9	3.2	ND	7.0	6.6
11	June 7	15.93	2.29	188.0	107.1	80.9	7.0	15.1	4.3	7.5	ND	ND
12	June 11	19.66	4.39	260.2	97.1	163.1	3.9	20.9	4.6	8.6	.9	5.2
13	June 12	34.69	1.01	323.7	27.7	296.0	1.2	7.4	ND	2.5	.7	1.6
15	June 18	24.06	2.87	261.3	77.0	184.3	4.7	15.2	ND	7.3	.5	2.1
18	July 22	5.72	14.17	234.4	144.3	90.1	13.1	34.0	7.4	19.9	1.7	4.6
19	July 23	22.72	3.46	150.1	97.3	52.8	6.9	21.8	4.7	8.7	1.0	4.7
21	July 28	22.39	7.88	326.8	216.6	110.2	13.7	36.5	10.0	19.4	1.1	4.8
22	Aug. 10	6,803.82	3.97	68.9	36.7	32.2	.6	10.0	.1	.8	.7	1.9
26	Sept. 14	15.65	.53	191.5	90.6	102.9	16.6	28.5	4.7	8.6	1.6	3.4
27	Sept. 21	3.49	1.56	492.3	154.7	337.6	62.3	29.8	6.6	16.8	12.4	17.8
28	Sept. 22	6.51	1.27	93.8	36.8	57.0	5.6	11.4	2.5	5.8	.8	3.7
30	Jan. 2	12.18	...	303.8	189.8	114.0	ND	8.1	8.4	17.9	10.6	11.6
31	Jan. 5	9.85	...	158.1	116.3	41.8	7.6	8.2	3.1	13.0	1.8	2.3
33	Feb. 20	23.95	...	259.1	136.6	122.5	49.9	3.7	3.6	10.9	10.5	5.3
34	Feb. 26	18.86	...	50.7	33.0	17.7	2.4	6.2	1.0	5.2	.9	.4
35	Feb. 28	91.35	...	22.4	13.2	9.2	1.1	2.7	5.5	1.9	.4	.6
39	Mar. 30	19.73	.12	87.0	54.3	32.7	3.9	10.1	2.3	7.5	1.3	1.6
1 year		7,531.51	3.67	71.6	37.4	34.2	1.0	9.6	.3	1.1	.8	1.9

TABLE 12

BASIC DATA FOR ONTARIO ALSIKE CLOVER SOIL PLOT 3: LOSSES OF SOIL AND WATER AND CONCENTRATIONS OF SOLUBLE CONSTITUENTS IN THE WATER OF 19 RUNOFFS DURING A 13-MONTH PERIOD 1938-39, WITH TOTAL LOSSES AND AVERAGE CONCENTRATIONS FOR 16 RUNOFFS DURING ONE YEAR APRIL 1, 1938, TO MARCH 31, 1939

Runoff		Soil loss (lbs./A)	Density washoff (lbs. soil /cu. ft.)	Total solids (ppm)	Ignited solids (ppm)	Loss on ignition (ppm)	Total N (ppm)	Ca (ppm)	Mg (ppm)	S (ppm)	K (ppm)	Na (ppm)
No.	Date											
1	Mar. 2	176.28	.01	43.6	28.3	17.3	ND	5.4	ND	ND	ND	ND
2	Mar. 5	15.95	.01	69.7	39.6	30.1	ND	4.8	1.1	ND	.6	2.6
3	Mar. 23	12.37	.78	132.6	91.7	40.9	1.9	2.4	2.9	ND	2.0	2.4
4	April 1	4.75	1.30	154.0	108.2	45.8	ND	7.3	3.8	ND	1.7	2.3
5	April 12	540.07	..	21.9	9.5	12.4	1.3	.7	.2	ND	.5	6.3
8	May 16	11.11	.07	243.9	162.5	81.4	15.7	4.7	4.9	ND	6.0	5.1
11	June 7	4.84	5.93	295.3	76.1	219.2	6.0	18.6	2.7	10.6	2.2	2.3
12	June 11	3.51	.65	118.3	58.6	59.7	ND	18.9	1.2	ND	.8	1.3
17	July 14	5.06	.95	374.7	207.3	167.4	10.7	43.7	15.4	17.3	18.4	31.2
21	July 28	5.64	1.01	123.1	62.2	60.9	5.3	14.6	2.1	9.5	2.0	2.2
22	Aug. 10	1,231.29	.16	37.4	21.6	15.8	.6	4.9	.3	.9	1.1	1.9
23	Aug. 30	5.13	.10	135.1	47.2	87.9	8.0	12.9	4.1	5.0	4.3	.0
26	Sept. 14	5.04	.69	144.2	72.0	72.2	17.5	16.4	5.9	7.6	7.3	3.5
30	Jan. 2	60.90	...	131.7	72.4	59.3	ND	3.6	4.2	8.0	11.8	7.7
31	Jan. 5	144.23	...	61.9	38.9	23.0	1.7	ND	ND	ND	ND	ND
33	Feb. 20	17.56	...	212.2	119.6	92.6	29.0	6.5	4.7	13.2	10.9	5.1
34	Feb. 26	3.06	...	ND	ND	ND	8.1	ND	ND	ND	ND	ND
35	Feb. 28	32.85	...	58.0	24.3	33.7	16.4	4.1	.7	2.5	2.4	1.3
39	Mar. 30	7.80	.32	116.6	66.4	50.2	9.3	7.5	22.7	9.7	2.3	1.9
1 year		2,082.84	.12	43.6	24.1	19.5	1.6	3.9	.6	1.6	1.5	3.4

TABLE 13

BASIC DATA FOR ONTARIO SOYBEAN PLOT 4: LOSSES OF SOIL AND WATER AND CONCENTRATIONS OF SOLUBLE CONSTITUENTS IN THE WATER OF 16 RUN-OFFS DURING A 13-MONTH PERIOD 1938-39, WITH TOTAL LOSSES AND AVERAGE CONCENTRATIONS FOR 13 RUN-OFFS DURING ONE YEAR APRIL 1, 1938, TO MARCH 31, 1939

Runoff		Soil loss (lbs./A)	Density washoff (lbs. soil /cu. ft.)	Total solids (ppm)	Ignited solids (ppm)	Loss on ignition (ppm)	Total N (ppm)	Ca (ppm)	Mg (ppm)	S (ppm)	K (ppm)	Na (ppm)
No.	Date											
1	Mar. 2. . . . .	11.22	.01	82.0	38.3	43.7	ND	8.4	ND	ND	ND	ND
2	Mar. 5. . . . .	48.07	.01	58.8	26.9	31.9	ND	4.4	2.3	ND	.8	2.0
3	Mar. 23. . . . .	5.10	.12	166.3	87.1	79.2	ND	ND	ND	ND	ND	ND
4	April 1. . . . .	2.83	.07	151.0	82.4	71.6	ND	15.2	6.6	ND	3.5	3.9
5	April 12. . . . .	560.90	. .	23.1	9.8	13.3	1.9	.8	.2	ND	.3	.9
8	May 16. . . . .	4.33	.02	151.0	99.2	51.8	19.1	7.7	1.3	ND	4.8	6.7
12	June 11. . . . .	6.98	8.94	712.7	399.9	312.8	16.8	51.9	21.2	ND	7.9	29.1
13	June 12. . . . .	6.81	4.53	337.0	79.3	257.7	4.8	12.4	ND	11.9	1.6	5.1
15	June 18. . . . .	5.85	4.56	ND	ND	ND	32.9	ND	ND	ND	ND	ND
17	July 14. . . . .	5.40	4.34	230.5	123.6	106.9	11.6	32.2	8.0	16.1	4.1	13.3
22	Aug. 10. . . . .	86.83	.34	52.9	26.9	26.0	1.4	7.2	.7	1.4	1.1	2.4
31	Jan. 5. . . . .	20.92	. .	300.5	168.5	132.0	26.1	2.6	17.9	12.5	10.8	32.0
33	Feb. 20. . . . .	23.23	. .	ND	ND	ND	ND	ND	ND	ND	ND	ND
34	Feb. 26. . . . .	32.05	. .	94.3	37.4	56.9	20.3	3.9	3.1	3.5	6.6	1.7
35	Feb. 28. . . . .	19.17	. .	87.9	45.4	42.5	12.2	6.5	.7	3.7	1.8	6.1
39	Mar. 30. . . . .	7.96	.87	109.9	60.0	49.9	8.2	12.3	5.2	8.9	3.1	3.0
1 year . . . . .		783.26	.24	51.7	24.6	27.1	4.1	2.9	1.2	4.5	1.1	2.5

TABLE 14

BASIC DATA FOR ONTARIO CONTINUOUS FALLOW PLOT 5: LOSSES OF SOIL AND WATER AND CONCENTRATIONS OF SOLUBLE CONSTITUENTS IN THE WATER OF 32 RUNOFFS DURING A 13-MONTH PERIOD 1938-39, WITH TOTAL LOSSES AND AVERAGE CONCENTRATIONS FOR 29 RUNOFFS DURING ONE YEAR APRIL 1, 1938, TO MARCH 31, 1939

Runoff		Soil loss (lbs./A)	Density washoff (lbs. soil /cu. ft.)	Total solids (ppm)	Ignited solids (ppm)	Loss on ignition (ppm)	Total N (ppm)	Ca (ppm)	Mg (ppm)	S (ppm)	K (ppm)	Na (ppm)
No.	Date											
1	Mar. 2	49.67	.01	39.9	21.4	18.5	ND	5.4	ND	ND	ND	ND
2	Mar. 5	167.01	.47	42.0	22.8	19.2	ND	5.6	1.6	ND	1.2	4.0
3	Mar. 23	71.98	2.89	105.0	64.6	40.4	2.7	4.7	4.1	ND	.8	2.9
4	Apr. 1	595.81	8.09	61.2	37.3	23.9	2.1	9.4	2.7	ND	.3	1.6
5	Apr. 12	769.23	5.29	13.5	8.1	5.4	.9	.6	.1	ND	.1	.9
6	Apr. 13	391.47	5.29	35.7	33.4	22.3	1.2	.9	.6	ND	ND	ND
7	Apr. 22	12.12	1.52	110.2	65.0	45.2	2.1	1.0	3.7	ND	ND	ND
8	May 16	4.30	4.79	275.2	188.6	86.6	11.5	12.0	7.1	ND	3.7	8.5
11	June 7	102.37	2.07	79.2	55.8	23.4	3.1	10.3	2.6	5.1	1.1	3.8
12	June 11	624.7	7.39	451.4	189.4	262.0	5.1	27.1	10.0	7.4	2.0	10.8
13	June 12	84.54	2.04	108.4	34.1	74.3	ND	6.5	ND	3.9	.7	2.2
14	June 17	252.96	2.92	663.2	130.2	533.0	7.0	31.9	ND	22.6	1.3	3.7
15	June 18	160.36	4.95	566.3	119.7	446.6	6.4	17.2	ND	16.8	1.9	8.1
17	July 14	6.33	10.15	293.3	173.2	120.1	12.4	45.2	8.9	26.5	1.6	12.0
18	July 22	17.02	4.66	186.1	124.6	61.6	5.9	26.5	6.3	13.4	1.2	4.2
19	July 23	101.69	3.49	187.0	119.8	67.2	8.4	18.2	6.7	13.0	1.1	6.0
20	July 25	5.63	5.37	502.2	362.1	140.1	17.3	65.3	17.8	56.2	2.1	8.0
21	July 28	77.59	5.91	539.3	402.7	136.6	17.2	45.8	19.4	30.7	2.6	9.6
22	Aug. 10	8,712.52	5.49	50.6	33.8	16.8	.6	7.4	1.6	1.0	.3	2.1
23	Aug. 30	21.57	4.61	87.5	43.1	44.4	4.8	11.6	2.9	4.1	1.1	1.1
24	Sept. 7	44.24	.90	65.0	28.3	36.7	4.4	8.2	2.2	2.6	1.6	.3
25	Sept. 12	10.29	1.21	123.1	60.3	62.9	4.5	14.5	4.1	7.4	1.0	1.2
26	Sept. 14	566.48	1.15	38.0	19.2	18.8	.8	5.4	1.6	1.1	.5	.6
27	Sept. 21	191.47	.27	27.4	14.0	13.4	1.9	4.1	.7	1.3	.5	2.2
28	Sept. 22	36.64	.37	37.7	18.3	19.4	2.1	5.3	1.3	1.3	.6	2.3
30	Jan. 2	15.48	1.28	292.0	107.2	94.8	11.8	10.8	6.1	11.8	6.5	10.0
31	Jan. 5	5.61	1.28	228.8	142.0	86.8	30.2	15.7	6.2	19.4	7.4	4.9
33	Feb. 20	72.12	...	103.0	73.1	29.6	4.7	13.5	3.0	8.8	.8	2.2
34	Feb. 26	19.21	...	26.9	11.9	12.0	1.5	3.6	.8	2.3	.4	.6
35	Feb. 28	21.80	...	32.1	21.7	10.7	1.2	4.4	3.4	2.3	.2	.6
37	Mar. 25	163.30	.06	21.0	11.3	9.7	6.5	2.7	.6	1.4	.3	.5
39	Mar. 30	23.58	.57	61.7	44.9	19.8	3.9	9.1	2.1	4.7	.6	1.3
1 year		12,491.84	4.71	61.3	37.3	26.9	1.3	7.4	1.8	2.0	.4	2.2

TABLE 15

BASIC DATA FOR ONTARIO BLUEGRASS SOIL PLOT 6: LOSSES OF SOIL AND WATER AND CONCENTRATIONS OF SOLUBLE CONSTITUENTS IN THE WATER OF 12 RUNOFFS DURING A 13-MONTH PERIOD 1938-39, WITH TOTALS AND MEANS FOR 10 RUNOFFS DURING ONE YEAR APRIL 1, 1938, TO MARCH 31, 1939

Runoff		Water volume (cu. ft./A)	Soil loss (lbs./A)	Density washoff (lbs. soil /cu. ft.)	Total solids (ppm)	Ignited solids (ppm)	Loss on ignition (ppm)	Total N (ppm)	Ca (ppm)	Mg (ppm)	S (ppm)	K (ppm)	Na (ppm)
No.	Date												
1	Mar. 2.....	1,522.39	2.9	.01	44.8	18.4	26.4	ND	3.9	ND	ND	ND	ND
2	Mar. 5.....	1,666.45	13.5	.01	36.4	15.4	21.0	ND	3.4	.8	ND	.1	2.6
4	April 1.....	9.76	.2	.02	94.8	47.3	47.5	5.1	4.9	1.2	ND	.8	3.1
5	April 12.....	304.49	.0	...	21.8	9.1	12.7	.6	.6	.1	ND	.2	1.7
11	June 7.....	4.44	20.7	4.66	463.4	126.3	337.1	41.5	24.8	3.6	36.3	11.7	7.3
22	Aug. 10.....	146.43	9.6	.07	30.8	13.6	17.2	ND	3.1	.5	1.1	.8	2.1
30	Jan. 2.....	32.05	.0	...	157.8	103.0	52.8	15.5	4.6	3.0	9.8	11.7	5.4
31	Jan. 5.....	11.10	.0	...	110.1	68.9	41.2	3.9	8.8	2.8	8.9	4.9	2.0
33	Feb. 20.....	38.46	.0	...	85.1	49.1	36.0	5.1	6.6	1.6	6.5	3.5	2.0
34	Feb. 26.....	10.50	.0	...	61.8	34.1	27.7	5.6	5.1	1.5	5.1	2.2	1.2
35	Feb. 28.....	68.11	.0	...	29.5	16.2	13.4	1.8	2.4	1.4	1.9	.9	.9
39	Mar. 30.....	17.91	.0	...	76.1	41.6	34.5	3.2	5.5	1.3	5.3	2.1	1.1
1 year ....		643.25	30.5	.05	13.1	21.8	21.3	2.8	2.5	.7	3.9	1.4	2.0

TABLE 16

BASIC DATA FOR DUNKIRK CONTINUOUS FALLOW PLOT 7: LOSSES OF SOIL AND WATER AND CONCENTRATIONS OF SOLUBLE CONSTITUENTS IN THE WATER OF 37 RUNOFFS DURING A 13-MONTH PERIOD 1938-39, WITH TOTALS AND MEANS FOR 34 RUNOFFS DURING ONE YEAR APRIL 1, 1938, TO MARCH 31, 1939

Runoff		No.	Date	Water volume (cu. ft./A)	Soil loss (lbs./A)	Density washoff (lbs. soil /cu. ft.)	Total solids (ppm)	Ignited solids (ppm)	Loss on ignition (ppm)	Total N (ppm)	Ca (ppm)	Mg (ppm)	S (ppm)	K (ppm)	Na (ppm)
1	Mar. 2	1	Mar. 2	1,559.91	161.9	.10	41.2	21.0	20.2	ND	4.0	ND	ND	ND	ND
2	Mar. 5	2	Mar. 5	1,048.07	600.6	.57	54.1	27.3	26.8	ND	6.0	ND	ND	7	ND
3	Mar. 23	3	Mar. 23	22.70	33.6	1.48	248.2	143.1	105.1	14.7	9.7	7.6	ND	1.1	5.5
4	April 1	4	April 1	90.81	533.7	5.87	71.8	47.6	27.2	3.5	7.0	2.4	ND	1.1	1.6
5	April 12	5	April 12	4,215.54	950.4	.23	94.3	45.3	49.0	4.9	.8	2.0	ND	.5	2.5
6	April 13	6	April 13	185.07	451.9	2.44	75.3	43.3	32.0	4.0	.5	1.6	ND	ND	ND
7	April 22	7	April 22	21.59	12.6	.58	105.1	59.6	45.5	ND	.9	2.9	ND	ND	ND
8	May 16	8	May 16	13.47	14.2	1.05	162.7	96.2	66.5	6.5	4.4	3.3	ND	1.3	3.9
9	May 29	9	May 29	70.1	5.88	1.95	108.7	108.7	86.8	9.3	22.6	5.1	ND	.9	3.0
10	June 2	10	June 2	12.5	2.18	129.8	68.3	61.5	8.0	8.0	19.6	5.9	ND	.8	2.3
11	June 7	11	June 7	39.50	345.4	8.49	187.6	59.0	127.8	9.0	14.8	3.1	9.1	.9	3.7
12-13	June 11-12	12-13	June 11-12	50.40	170.1	9.37	247.7	46.0	201.7	3.3	12.5	ND	4.3	.8	3.6
15	June 18	15	June 18	52.18	361.0	6.87	255.9	52.2	203.7	3.6	12.1	ND	6.3	.9	1.9
16	July 11	16	July 11	11.97	25.6	2.14	97.4	63.4	34.0	5.4	16.5	2.6	6.9	2.0	3.4
17	July 14	17	July 14	38.81	229.3	5.91	130.4	61.1	78.3	10.3	18.3	4.2	6.1	.7	5.1
18	July 22	18	July 22	17.19	39.8	2.31	136.5	95.0	41.5	8.9	19.6	4.5	9.4	2.5	3.3
19	July 23	19	July 23	30.21	115.2	3.69	133.1	80.7	52.4	7.9	16.0	4.4	5.7	1.4	4.5
20	July 25	20	July 25	94.59	397.4	4.20	178.1	85.5	92.6	16.6	21.3	5.6	8.8	1.0	7.3
21	July 28	21	July 28	11.21	119.8	13.36	395.6	166.0	229.6	53.9	45.7	10.4	18.9	2.7	8.7
22	Aug. 10	22	Aug. 10	10,457.36	91,557.0	8.75	34.0	17.8	16.2	1.5	3.1	1.1	1.0	.3	1.0
23	Aug. 30	23	Aug. 30	5.40	94.4	17.48	216.7	89.9	126.8	26.1	23.0	5.8	11.3	6.1	2.3
24	Sept. 7	24	Sept. 7	18.02	43.7	2.43	67.7	29.4	38.3	9.6	8.7	2.1	3.0	1.1	.7
25	Sept. 12	25	Sept. 12	12.38	15.2	1.23	72.2	35.9	36.4	4.8	10.5	2.6	4.0	.9	1.1
26	Sept. 14	26	Sept. 14	70.13	123.8	1.77	42.1	21.9	20.2	2.2	3.8	1.6	1.7	.5	.8
27	Sept. 21	27	Sept. 21	55.52	35.5	.64	73.1	36.9	36.5	9.6	8.7	2.2	2.9	2.0	5.1
28	Sept. 22	28	Sept. 22	14.55	1.9	.13	45.2	23.2	22.0	2.5	6.6	1.6	1.9	.7	2.7
29	Nov. 19	29	Nov. 19	9.12	.5	.05	542.9	175.7	367.2	88.4	9.5	9.5	14.9	29.8	17.2
30	Jan. 2	30	Jan. 2	17.18	.0	...	136.1	86.2	50.2	10.8	5.6	5.0	9.4	5.9	7.7
31	Jan. 5	31	Jan. 5	160.17	5.5	.03	92.2	58.1	34.1	5.4	10.7	3.2	7.6	1.6	2.4
32	Feb. 13	32	Feb. 13	608.97	.0	...	40.9	20.4	20.5	4.4	3.5	.8	3.0	.9	1.0
33	Feb. 20	33	Feb. 20	4,727.49	4.4	.01	117.5	61.2	56.3	12.7	11.1	4.1	5.1	.6	3.3
34	Feb. 26	34	Feb. 26	512.71	6.7	.01	26.3	14.4	11.9	1.9	3.5	.8	5.0	.7	1.4
35	Feb. 28	35	Feb. 28	400.36	17.8	.04	128.4	69.6	58.8	15.1	19.5	.5	6.3	.7	3.5
36	Mar. 5	36	Mar. 5	1,443.91	900.0	.62	92.9	52.6	40.3	9.5	12.7	.7	4.8	.7	1.4
37	Mar. 25	37	Mar. 25	2,362.86	1,057.3	.15	50.2	26.6	23.6	9.2	6.7	1.7	3.3	.3	1.2
38	Mar. 27	38	Mar. 27	532.28	185.7	1.23	106.9	52.3	54.6	24.6	14.4	3.5	5.8	.8	2.0
39	Mar. 30	39	Mar. 30	1,063.93	1,310.7	1.23	71.6	32.5	39.1	3.6	7.3	2.0	2.5	.4	1.5
1 year				27,362.38	99,229.1	3.63	70.1	35.7	34.4	6.1	5.9	1.5	2.9	.5	1.9

TABLE 17

BASIC DATA FOR DUNKIRK ALFALFA-CORN, PLOT 8: LOSSES OF SOIL AND WATER AND CONCENTRATIONS OF SOLUBLE CONSTITUENTS IN THE WATER OF 36 RUNOFFS DURING A 13-MONTH PERIOD 1938-39, WITH TOTAL LOSSES AND AVERAGE CONCENTRATIONS FOR 33 RUNOFFS DURING ONE YEAR APRIL 1, 1938, TO MARCH 31, 1939

Runoff		Soil loss (lbs./A)	Density washoff (lbs. soil /cu. ft.)	Total solids (ppm)	Ignited solids (ppm)	Loss on ignition (ppm)	Total N (ppm)	Ca (ppm)	Mg (ppm)	S (ppm)	K (ppm)	Na (ppm)
No.	Date											
1	Mar. 2	1,602.08	.02	28.0	14.4	13.6	ND	4.1	ND	ND	ND	ND
2	Mar. 5	2,122.28	.03	39.1	18.1	21.0	ND	4.2	1.0	ND	1.0	2.8
3	Mar. 23	8.33	.73	176.7	113.8	62.9	7.2	5.0	1.4	ND	3.9	8.4
4	April 1	6.39	.05	130.8	83.7	47.1	6.0	5.1	2.4	ND	3.0	2.8
5	April 12	4,484.94	.03	25.3	25.3	27.4	3.1	5.5	1.2	ND	1.1	1.2
6	April 13	249.52	.52	111.3	59.4	51.9	5.6	.6	2.9	ND	ND	ND
7	April 22	46.94	.44	144.8	76.8	68.0	6.9	.6	3.4	ND	ND	ND
8	May 16	12.39	.73	214.1	111.9	102.5	23.3	ND	ND	ND	ND	ND
9	May 29	12.59	3.18	181.2	105.9	75.1	10.9	29.5	.9	ND	.9	5.2
10	June 2	5.86	2.58	139.6	69.1	70.5	7.3	24.9	3.2	ND	1.0	1.9
11	June 7	25.33	13.11	223.2	93.5	129.7	8.0	23.1	4.1	7.6	1.3	5.9
12-13	June 11-12	22.83	3.34	135.9	180.8	255.1	20.5	40.8	ND	14.8	4.2	14.4
15	June 18	27.71	8.44	545.4	287.0	258.4	20.9	53.8	ND	26.4	3.8	10.4
16	July 11	17.53	1.05	107.4	70.4	37.0	5.2	33.7	2.4	6.9	1.8	5.7
17	July 14	24.46	5.74	397.2	227.5	169.7	25.0	44.7	10.4	26.0	2.0	12.4
18	July 22	10.53	1.31	393.3	282.7	110.6	21.2	53.7	8.7	28.4	3.1	8.6
19	July 25	17.26	1.60	331.7	224.8	109.9	21.1	46.9	8.6	16.6	2.0	12.0
20	July 25	24.24	1.67	454.9	315.4	139.1	ND	41.2	11.1	18.1	2.2	10.7
21	July 28	6.06	5.20	765.1	525.3	239.8	46.1	112.8	19.4	64.8	3.0	20.4
22	Aug. 10	4,489.94	3.47	16.2	28.0	18.2	2.4	5.7	.3	2.1	.5	2.0
23	Aug. 30	6.06	9.83	276.8	161.0	115.8	36.3	35.4	6.2	28.5	7.6	3.0
24	Sept. 7	6.05	3.54	58.3	57.1	8.0	8.0	16.9	2.6	9.1	2.5	.1
25	Sept. 12	3.60	1.11	1,274.9	141.0	1,133.9	ND	32.7	6.2	16.8	9.2	4.1
26	Sept. 14	8.84	1.40	145.1	77.0	68.1	5.8	19.8	4.0	9.4	3.0	3.4
27	Sept. 21	18.55	.53	148.3	84.4	63.9	15.8	11.4	3.1	7.0	8.8	14.5
29	Nov. 19	5.59	.02	345.2	161.3	180.9	65.9	15.6	10.5	20.5	24.6	15.6
30	Jan. 2	38.46	...	129.9	76.1	53.5	10.0	4.7	4.5	8.1	6.0	7.9
31	Jan. 5	75.32	...	129.1	80.1	49.0	10.2	11.8	5.2	11.0	4.1	6.2
32	Feb. 13	60.90	.01	109.7	61.6	48.1	7.6	1.6	1.2	8.7	3.4	1.5
33	Feb. 20	2,724.22	...	246.1	135.5	90.6	18.4	17.2	ND	10.6	1.3	12.1
34	Feb. 26	30.45	...	62.4	38.8	23.6	3.8	6.5	ND	2.1	.3	.1
35	Feb. 28	73.72	...	33.7	19.7	14.0	.9	4.2	5.2	2.8	.2	.7
36	Mar. 5	1,680.25	.09	223.2	145.0	78.2	17.3	23.3	9.0	9.7	1.1	1.3
37	Mar. 25	174.89	.50	197.4	118.6	78.8	18.7	19.7	7.3	8.6	1.2	1.6
38	Mar. 27	656.51	.05	280.7	173.2	107.5	28.3	30.7	10.0	11.8	1.4	14.3
39	Mar. 30	1,522.67	.22	227.7	124.7	103.0	15.4	28.6	.8	11.2	1.4	8.5
1 year		16,570.60	1.07	132.9	79.2	53.7	9.5	11.6	3.5	7.4	.8	4.6





## APPENDIX B

### DESCRIPTIVE SUMMARY OF WEATHER AND SOIL CONDITIONS IN RELATION TO INDIVIDUAL RUNOFFS

*January — February, 1938*, had been characterized by frequent rains and thaws following a very wet autumn in 1937. The net result must have been an incompletely and only intermittently frozen soil and a rather complete removal of soluble materials by both leaching and runoff.

*March, 1938*, was a month of abnormally warm weather. A thaw on the 2nd caused the first runoff from which samples were taken for analysis. A 0.32 inch rain on the 5th removed the remaining snow and caused a large runoff. Two weeks of unusually warm weather followed, culminating on the 23rd in a 0.32 inch rain, the first high intensity rain of the season. The small runoff was of generally high salt concentration. It is probable that the soil had thawed and dried sufficiently by this time to allow evaporation of water from and rise of soluble salts to the surface. A week of cooler and more seasonable weather occurred before the next rain, March 31. The resulting runoff was collected April 1. The Ontario gauge recorded 0.36 inches with a maximum 5-minute intensity of 2.04 inches per hour, while the Dunkirk gauge recorded 0.30 inches with a maximum 5-minute intensity of 1.44 inches. This difference was reflected in much smaller soil, water, and soluble material losses from the fallow Dunkirk plot than from the fallow Ontario plot.

*April, 1938*, was characterized first by cold wintry weather and heavy snowfall, culminating on the 12th in a sudden thaw with large runoffs from all plots. The 0.18 inch rain on the 13th thus fell on wholly saturated soil. Both runoffs were very dilute. The rest of April was very warm with practically no rain except for a 0.72 inch rain of rather low intensity on the 22nd which caused small runoffs from only three plots. The first working of the soil on any of the plots was done on the 20th, when the fallow plots were spaded.

*May, 1938*, was a month of less than average rainfall. There were five distinct rains, all less than 0.80 inch, of which only two (May 14–15, and 29) were effective in causing runoff from any of the erosion plots. Only the last one was of high intensity.

The May 14–15 rain, of low intensity but long duration, caused uniformly small runoffs from nearly all plots. It fell after five days of subnormal temperatures and no rain, during which period evaporation and salt rise had probably been slight. Low intensity rains of 0.34 inch on the 20th and 0.40 inch on the 24th caused no runoff. Cultivation of the four currently fallow plots May 17 and 19 may have been the dominant factor in preventing any runoff as a result of these two rains by increasing the absorption capacity of the bare soil.

The shower on the 29th is worthy of note because of the great differences in its amount and intensity at the two series of plots. The Ontario gauge recorded 0.18 inch with a maximum 5-minute intensity of 0.72 inch, while the Dunkirk gauge recorded 0.46 inch of rain with a maximum 5-minute intensity of 3.60 inches per hour. None of the Ontario plots underwent runoff loss, but both Dunkirk plots suffered some erosion with relatively high soil loss and high soluble salt concentration in runoff water.

*June, 1938*, rainfall occurred mostly during the period from the 2nd to the 19th in the form of six high intensity rains, all of which caused runoff from at least some of the erosion plots. During this period temperatures were above normal and the rains were spaced closely enough to keep the soil quite moist. These June runoffs

all carried a fairly high concentration of soluble materials, due in part to the comparatively small amounts of runoff in any case and also probably to the rapid rise of soluble salts to the soil surface during the short but hot drying periods between rains.

A 0.55 inch rain of moderate intensity on June 2 caused light runoff only from the Dunkirk plots and none from the Ontario plots in spite of the fact that the rainfall intensity curve was practically the same at both sites. This probably reflected the greater porosity of the Ontario loam as compared to the Dunkirk silty clay loam. The 0.74 inch rain on the afternoon of June 7 followed five days of uniformly warm weather. It was of very high initial intensity, the 5-minute maximum rate of 3.60 inches per hour occurring at the start. Soil and water losses occurred in considerable amounts from all except two of the plots. This rain afforded an opportunity to observe the effect of fertilizer upon the loss of soluble salts in the first runoff water after application, because it fell only a few hours after liberal applications of 5-10-5 to the currently fallow Ontario Plots 2, 4, and 5.

On June 9-10 a 0.14 inch rain of low intensity caused no runoff. This rain is worthy of note, however, because it occurred only a few hours after Dunkirk Plot 8 had been fertilized and planted to corn, a circumstance which would tend to minimize the effect of fertilizer upon the first subsequent runoff from that plot on the 11th. A 0.24 inch rain of high intensity at 3 P.M. of the 11th caused soil and water losses from nearly all plots. On June 12 a 0.50 inch rain of several hours' duration and one period of high intensity resulted in considerable soil and water loss, especially from Ontario fallow Plot 5. Samples of the runoff on June 11 were taken only from the Ontario plots before the rain occurred the next day. As a result the samples of runoffs on June 11 and 12 from each of the two Dunkirk plots were composites.

July, 1938, rainfall was high but unevenly distributed throughout the month. A slow 0.24 inch rain on the 1st and a 0.15 inch shower on the 9th after a week without rain caused no runoff. A 0.65 inch shower of low intensity on the 11th caused small runoff from the Dunkirk plots only. The ensuing hot, drying weather, favorable for maximum evaporation and rise of soluble salts, was broken on the 14th by a 0.45 inch rain of high initial intensity. The rain caused considerable soil loss and runoff from the Dunkirk plots and a very small but concentrated runoff from four of the Ontario plots. Light rains on the 18th and 20th caused no runoff but were followed by a week of heavy rains, frequent runoffs, moist to saturated soil, consistently high temperatures, and very rapid evaporation and salt rise during the short intervals between rains. A 0.34 inch rain of high intensity on July 22-23 caused small runoff, and a 0.31 inch shower of high intensity on the afternoon of the 23rd caused considerably larger runoff because it fell on a nearly saturated soil. On the 25th a 0.14 inch shower of high intensity on the Ontario plots caused runoff only from fallow Plot 5, small in amount but high in soil content. The same shower on the Dunkirk plots was greater both in amount (0.44 inch) and intensity; consequently it caused considerable runoff of high soil content.

On the evening of July 28 a short intense shower caused runoff from five of the plots, including even Ontario soybean Plot 4 from which no runoff had occurred since July 14 because of the rapid growth of the soybeans to a dense protective cover. This rain followed three days of hot, drying weather and marked the climax of the July rainy period. The runoff was noteworthy because it carried an extremely high concentration of all of the soluble salts that appeared to be associated with the known high salt concentration in the surface  $\frac{1}{8}$  inch of fallow or nearly bare plot soils (Fig. 1).

August, 1938, weather was outstanding because of two facts: (a) the mean temperature and the total rainfall were both considerably above the average; (b) the 4.4 inch rain during 12 hours on August 10 was of about 100-year frequency and caused a great amount of erosion on the plots currently under poor cover.

The August 10 rain inevitably bulks large in this investigation. The maximum 5-minute rainfall of 0.54 inches at the rate of 6.48 inches per hour was of about 50-year frequency, and the maximum 2-hour rainfall of 2.78 inches from 10 to 12 P.M. was of from 25- to 50-year frequency for the north-central Finger Lakes region accord-

ing to the rainfall intensity—frequency charts of Yarnell (31). Runoff from this rain is considered in the main part of this paper (Table 4).

Light rains on the 17th, 22–23rd, and 25th caused no runoff. After several days of warm, clear weather a shower of high intensity on the 30th caused small runoffs from the fallow and corn plots.

*September, 1938*, was characterized by below normal temperatures and heavy rainfall of generally low intensity. A 0.22 inch rain on the 3rd caused no runoff. On the 7th a cool, gentle rain of nearly 0.60 inch saturated the soil but caused runoffs only from Ontario Plot 5 and the two Dunkirk plots. On the 12th a 0.34 inch rain of moderate intensity, after several days of fair weather, caused very small runoff from the same three plots.

The time from September 12 to 22 was the third really wet period of the 1938 growing season. Frequent rains were accompanied by cloudy skies and uniformly low temperatures conducive to low evaporation rates. These rains were of generally low intensities, and resulted in continuously very moist soil conditions. All these factors combined to cause runoffs not only large in volume but low in soil and in solute concentration.

On September 14–15 occurred a 1.02 inch rain of long duration and an intensity that was high at the maximum but very low on the average. It fell on soil still moist from the rain of the 12th and caused erosion on all plots except the soybean and bluegrass plots, with considerable soil and water loss from the fallow plots. Light rains on the 16th, 17th, and 19th kept the soil moist. A very steady 1.24 inch rain of low intensity on the 21st and another equally steady 0.49 inch rain on the 22nd reflected the western fringe of the hurricane then sweeping across New England. These two rains each caused moderately heavy runoffs from the fallow plots, and the first one also caused some from the corn plot. These washoffs carried an exceptionally large amount of fine material in suspension, possibly indicating some differential erosion by these unusually slow, steady, gentle rains. September 22 marked the end of the summer rains and the beginning of a dry, fair autumn.

*October, 1938*, was unusually dry and sunny, and after the first week was unseasonably warm. No runoffs occurred during October. From September 23 to November 8 the largest individual rainfall was 0.12 inch, on October 27.

*November, 1938*, was characterized by above normal temperatures, below normal precipitation, and only one small runoff. A 0.39 inch rain of low intensity on the 8th and a 0.36 inch rain on the 13th caused no runoff.

Runoff on November 18–19 from a 0.79 inch rain of low intensity was slight in amount, low in soil content, and occurred only on the Dunkirk plots. It carried a high concentration of some of the soluble constituents, as was to be expected in the first runoff after a long dry period. On November 23–24 about 5 inches of heavy wet snow fell on the unfrozen soil, followed by a period of zero temperature.

*December, 1938*, saw no runoff from the erosion plots. Before the 14th only light rains occurred, causing no runoff and doing little to raise the low level of ground water before winter freezing of the soil. A 0.29 inch rain on the 10th was the heaviest of the period. Leaching from it in the soil profile was probably too shallow to carry out in drainage water all of the salts, including nitrates, which had probably gradually accumulated during the autumn. Gradual freezing of the upper few inches of soil, accompanied by occasional light snows, characterized the remainder of the month.

*January, 1939*, precipitation occurred mainly as snowfall. Thaws on the 2nd and 5th caused small runoffs from most of the plots. The runoff on the 2nd was the first since September 22 or even earlier from the Ontario plots, and the first since November 19 from the Dunkirk plots. A 0.12 inch rain falling on bare ground on the 6th caused no runoff. Thereafter the soil froze to a depth of several inches and remained so until February 13. Snowfalls during January 13–18 and 30–31 provided complete snow cover for several weeks.

*February, 1939*, precipitation occurred mostly as snow during the latter half of the month. A thaw on the 13th caused runoff only from the Dunkirk plots. On the 19th and 20th rain and snow equivalent to 0.53 inches of water accompanied a thaw which caused flooded conditions throughout the Finger Lakes region. Runoff from

the Dunkirk plots was one of the heaviest of the year while the runoffs from the Ontario plots were uniformly much smaller in amount. A 0.33 inch rain of moderate intensity on the 22nd, following snowfall of the previous day, caused no runoff. On February 26-27 a thaw with snow and rain caused general runoff, again heavier from the Dunkirk plots than from the Ontario plots. A 0.14 inch rain on the 28th also caused general runoff. Soil loss during these runoffs was negligible.

*March, 1939*, weather conditions and erosion contrasted markedly with those of the unusually warm March, 1938. Precipitation was above normal and temperatures were normal. A 0.49 inch rain of low intensity on March 4-5 fell on bare soil and caused heavy soil and water loss from the Dunkirk plots but none from the others. During the next three weeks the soil remained frozen and for the most part was snow covered, while snow fell equivalent to 1.15 inches water. On the 25th a thaw resulted in large soil and water losses from Dunkirk fallow Plot 7 and smaller losses from Ontario fallow Plot 5 and Dunkirk corn Plot 8. The extremely oversaturated condition of the soil, especially on Plot 7, was probably responsible for the pronounced erosion in the absence of rain. On March 26-27 a 0.36 inch rain of low intensity fell on wholly thawed soil and caused heavy erosion on the Dunkirk plots but none on the Ontario plots. On the 30th a 0.58 inch rain fell on thoroughly saturated soil and caused heavy soil and water losses on both Dunkirk plots, in spite of its low intensity, but uniformly slight erosion from all Ontario plots regardless of plant cover.

## CONTENTS

Foreword.	LYLE F. WATTS	317
Professor G. B. MacDonald	RUSSELL E. GETTY, GEORGE B. HARTMAN, AND J. A. LARSEN	319
Survival and growth of various grades of shortleaf pine planting stock.	A. G. CHAPMAN	323
Cumulative tallying brought up to date.	CLARENCE D. CHASE	333
Lumber recovery from "woods waste" logs.	E. M. DAVIS	341
The small, low-income landholding: A problem in forest conservation.	WILLIAM A. DUERR	349
Forest products research in Oregon.	PAUL M. DUNN	363
Growth of tree plantings for erosion control in the southeastern region.	J. A. GIBBS	371
A range test of species adaptability.	RICHARD M. HURD	387
Judging range condition and trend in a range inventory project.	GEORGE W. KANSKY	395
Early researches in the relations of forest fires and unusual weather conditions, humidity, duff moisture, and inflammability.	J. A. LARSEN	405
Evaluation of tree risk in the spruce-fir region of the northeast.	THOMAS F. McLINTOCK	415
Diameter-growth studies of northern red oak and their possible silvicultural implication.	HAROLD F. SCHOLZ	421
Planting of water-tolerant trees along margins of fluctuating-level reservoirs.	T. H. SILKER	431
Influence of planted tree belt in Plainfield sand on erosion control and moisture conservation.	FRED B. TRENK	449

The Board of Editors of the *Iowa State College Journal of Science* dedicates this issue to Gilmour Byers MacDonald in recognition of service in forestry at the Iowa State College, 1907-1948.

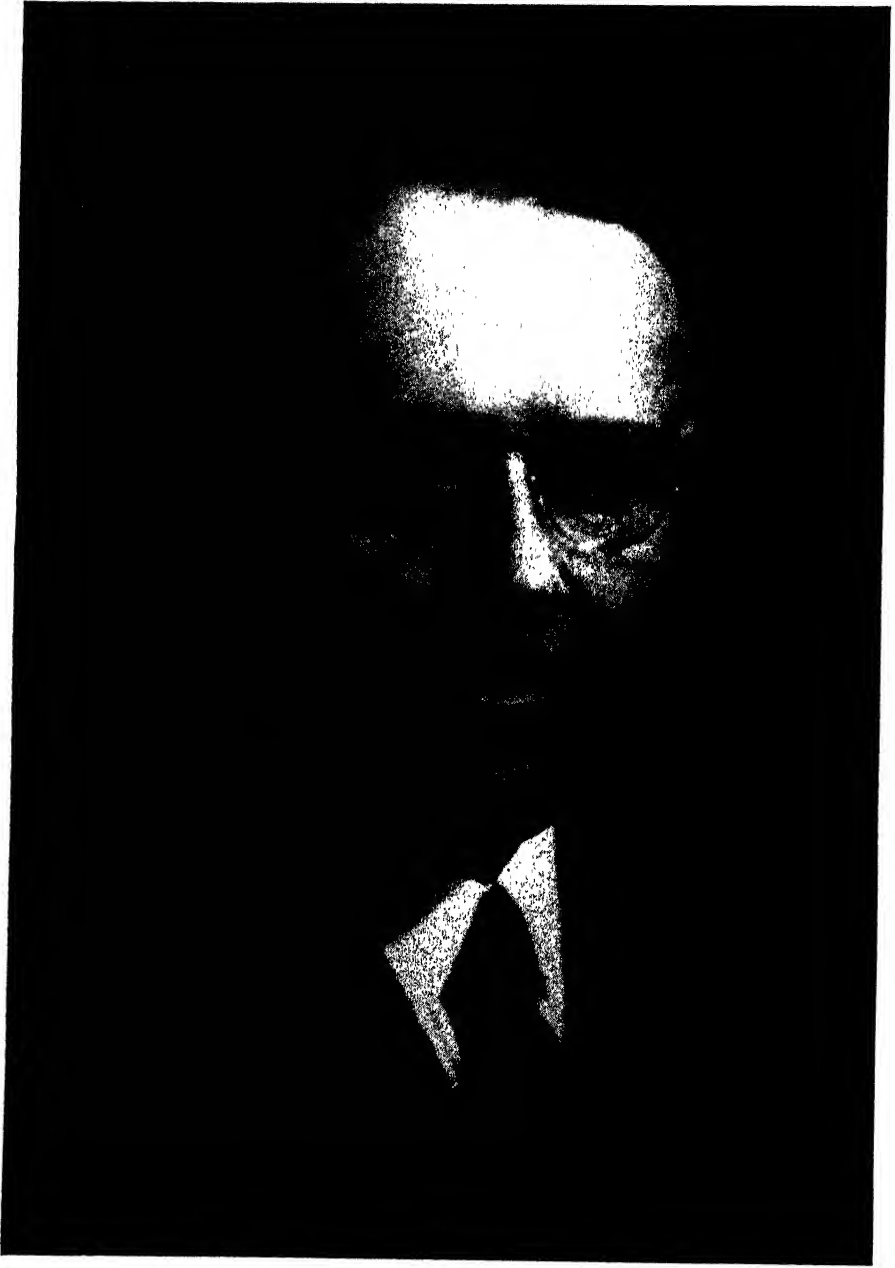
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GILMOUR BYERS MACDONALD

## FOREWORD

LYLE F. WATTS

*Chief, Forest Service, United States Department of Agriculture*

When a real leader in the profession retires from active duty, it is customary for the lesser lights to claim, "I knew him when." It is in that mood that I write this foreword.

I was one of the fortunate few who were studying forestry at Ames in 1910 when Professor Mac first took charge of forestry education at Iowa State College. We of that group found, as have the hundreds who have followed in forestry at Ames, that the new professor was a rare person. He was a splendid teacher with sound technical background and the ability to pass it on to others. But beyond that he had that exceptional talent to inspire his students to do good work, to live clean—in short, to be good citizens first of all.

Just as he influenced the lives of his students, so has he influenced the life of his adopted State. One has only to review the history of conservation in Iowa for the past forty years to realize that in large measure it mirrors the career of Professor MacDonald. It has been given to few foresters to lead his State in constructive progress for so long a period.

We forestry alumni of Iowa State College know that retirement as head of the Forestry Department will not interrupt the great work that Professor MacDonald has been doing. We expect that it simply means relief from details to permit an even greater contribution to the conservation movement in Iowa and in the Nation.



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Gilmour Byers MacDonald was born March 9, 1883, at Carleton, Nebraska. His father, a Scotchman, was a Presbyterian minister. His mother descended from a family named Piercy of English and Scotch ancestry. He had six brothers, three of whom are living. They are Kenneth, a missionary in the Philippine Islands, Rosmond who has a pulpit in Boston, and George of Pasadena, California. In the course of changing pastorates held by the father, the family moved to Hubbel, Hopewell, and Unandilla, Nebraska.

When Gilmour was in the fourth grade, the MacDonald family moved to Lincoln, Nebraska. At high school there, he became interested in athletics, especially track and football. This interest followed him through both high school and college. His football position was usually that of quarterback. In track, he was a pole vaulter and in this event he took first place at a dual track meet in Ames in 1906. During an interim of two years while attending the University of Nebraska, he worked in a fruit orchard and at retail merchandising in California. Upon his return to the University of Nebraska in 1904, he chose forestry as his life work and studied to that end. Entrance into the forestry field had been encouraged by Dr. G. E. Condra of the University. Gilmour graduated in 1907 with a B.S. degree in forestry. He earned a Master of Forestry degree at Nebraska in 1914.

It was while engaged at Halsey, Nebraska, the summer of 1905, that he first came in contact with forest nursery operations. This was evidently to his liking, for when upon graduation in 1907 he entered the United States Forest Service, much of his time was devoted to reforestation activities. On the Medicine Bow National Forest in Wyoming, he supervised the collection of three thousand bushels of pine cones. During the winter of 1907-08, while on detail in Washington, D. C., he prepared planting plans, among other activities. In 1908, he was given the assignment of starting the Pocatello Forest Nursery, and in 1910 he was in charge of the Boulder Forest Nursery, in Montana.

In 1910, he was married at Lincoln, Nebraska, to Edith Craig. Their children are two sons and two daughters. Captain Gilmour Craig MacDonald of the United States Army is now on the staff of the Ballistics Laboratory. He resides with his wife and two children at Cumberland, Maryland. Dr. Donald Craig MacDonald is associated with the United States Rubber Company at Passaic, New Jersey. He, his wife, and one child live in Ridgewood in the same state. Mary Janet, wife of Zac

Dunlap of the Dunlap Motor Company, lives in Ames, Iowa, Ruth Eloise, whose husband Robert Lamoreaux is employed by the Caterpillar Tractor Company, lives in Peoria, Illinois. All four children attended Iowa State College.

When Gilmour MacDonald returned to Lincoln from the West, he met an old friend, C. A. Scott, who was at that time teaching forestry at Iowa State College. Since Scott had accepted a position as State Forester of Kansas, he urged Gilmour to take over his teaching at Ames, at least temporarily. Prof. S. A. Beach, vice dean of Agriculture and head of the Department of Horticulture, was very favorably impressed with the young forester and his wife and offered a permanent position on the staff.

From the very beginning of his teaching career, Professor MacDonald realized the future possibilities in forestry for Iowa and the nation, and early concluded that one teacher in this line would never meet the need for expansion. That he correctly sensed the opportunities is well attested by the fact that at present the Iowa State College Department of Forestry, which he has so faithfully and efficiently headed, has now nine teachers and more than three hundred students. During the years he has consistently labored to improve instruction in forestry at Iowa State College until it now ranks among the foremost in the nation. In the intervening years he has also given active and constructive support to the organization and functioning of the Iowa Conservation Commission. He has held the office of State Forester for Iowa since 1935. He was the leader in the state's Civilian Conservation Corps program, and took the initiative in the establishment of the Iowa Forest Nursery; was a member of the Iowa State Planning Board and a leading contributor to the plans dealing with forestry and soil conservation embodied in the Iowa Twenty-Year Plan.

A devoted churchman, he holds several important offices and has been honored by a life position of elder of his church. He has been a city councilman of Ames for many years, a Rotarian, and Boy Scout leader of note. He is the recipient of the honorary Boy Scout Beaver Award.

For several years, he was a member of the Executive Council of the Society of American Foresters, which organization recently honored him by election to the grade of Fellow. In 1947, as fitting recognition for a life devoted to teaching and public service and in appreciation of his esteemed personal qualities, inspired leadership, and notable accomplishments, his Alma Mater, the University of Nebraska, conferred on him the degree of Doctor of Agriculture. Then in the spring of 1948, he was honored by being named by the Secretary of Agriculture to a newly-created 3-man National Forests Board of Review.

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## SURVIVAL AND GROWTH OF VARIOUS GRADES OF SHORLEAF PINE PLANTING STOCK

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The quality of planting stock is one of the chief factors to be considered in forest planting work. Strong planting stock grows more rapidly and vigorously than weak, and is better able to survive vegetational competition and endure late summer drouths. Since fewer high-grade seedlings or transplants are needed per acre to secure an adequate stocking, effective planting costs are less when high-grade stock is used than when ungraded or low-grade stock is used. For these reasons planting stock grades should be defined and tested in field plantings, from which their value can be determined.

Planting stock grades should be based on ability to grow under field conditions. Initially at least, separate grades should be recognized for species. If, upon investigation, certain species have similar survival and growth habits in plantations, they can be combined for grading purposes. Within a species group the different grades should show different survival and growth rates, depending upon the vigor of the individual. Grades must be based upon characteristics that are significant, easily identified, and economically suited to nursery grading and field planting.

### STOCK GRADES AND METHODS OF TESTING

During the three-year period from 1939 to 1941, one system of stock-grading was tested with 1-0 shortleaf pine planting stock. This stock, obtained from Forest Service nurseries in Missouri, Indiana, and Arkansas, was graded on the basis of length of stem above the root collar, and diameter of stem one inch above the root collar. Survival and growth of the seedlings were tested in spring plantings on poorer-than-average old-field sites on the Ozark, Clark, Hoosier, and Wayne National Forests. The chief purpose of this field testing was to determine any differences in survival and height growth on the part of seedlings of various heights and stem calipers. If significant differences were found to exist, seedling height and stem caliper might serve as a basis by which nurserymen could grade their stock to insure better field performance.

Seedling height classes were established in multiples of three or four inches, depending upon the range of seedling heights in the lot of nursery-run stock under study. That is, if seedlings in a nursery did



not exceed 10-inch heights in sufficient numbers to provide test stock, two 3-inch height classes, 4-7 and 7-10, were used. If 12-inch and taller stock were available, two 4-inch classes, 4-8 and 8-12, were used. The mean seedling height within each class was near the middle, except in the tallest height class, where the mean was somewhat below the midpoint.

Seedling caliper classes were established in twentieth-inch units. The 2/20-inch class, for example, contained trees having diameters from 1.5/20 to 2.5/20 inch. Within each height class, as many caliper classes were established as the caliper range of the stock permitted.

For the purpose of this study a stock grade includes seedlings within a given height and stem-caliper class. No seedling less than 4 inches high or having a stem less than 1.5/20 inch in diameter was included in any grade. These selected limits stay well below the smallest seedlings acceptable for field planting. All seedlings with poor or broken roots were culled.

It was recognized that quality of root system, degree of lignification of stem, and other factors influence survival and early growth of field-planted stock. These characteristics are too difficult to measure and describe to be of much practical value in stock grading. Although not specifically used to establish grades, neither quality of the root system nor stem lignification was completely ignored in the system of grading and culling used in this study. It is well known that sturdy, high-caliper seedlings are more likely to have better lignified stems, better developed roots and tops, and greater food reserves than tall slender ones. Better developed root systems, too, are associated with the sturdy seedlings. Seedlings with damaged roots, with roots less than 8 inches, or with long "rat-tail-like" roots without laterals were automatically culled in accordance with established practices of the nurseries involved. Roots longer than eight inches were pruned to this length before planting.

Ideally, all recognized grades of stock should have been tested each year for each nursery. This was not possible because of differences in quality of stock caused by variations in nursery soil, growing season, and other conditions affecting growth. Most of the grades were produced in all nurseries and tested in all four states.<sup>1</sup>

Another phase of the study included the analysis of the nursery-run of the stock at the three nurseries, during two years at two of them, to determine the proportions of the stock falling into each of the grades being studied.

## RESULTS AND DISCUSSION

Experimental results are summarized in Tables 1, 2, and 3. Table 1 shows survival percentage and height growth in feet in relation to (1) stock grades, (2) height class alone, (3) caliper class alone, and (4)

<sup>1</sup> Tests of relative values of stock grades from each nursery were made each year in Latin Squares but did not include tests of differences among nurseries, among sites, or among parts of the region. The Latin Square is a convenient, effective design, particularly adapted to testing differences in nursery stock in field plantings.

height-caliper ratio. Of primary importance in field planting is the establishment of the stand, and this, first of all, depends upon survival. Therefore, in grading the stock, in this study, more emphasis was placed upon survival than upon height growth. Superior height increment for any stock grade is practically significant only when that superiority, during the first few years, (1) better adapts the seedling for survival in competing vegetation, (2) leads to earlier dominance, (3) results in

TABLE 1

AVERAGE SURVIVAL AND HEIGHT INCREMENT OF SHORTLEAF PINE PLANTING STOCK OF VARYING HEIGHT AND CALIPER CLASS

Plot Number	Year of Establishment and State	Height Class	Caliper Class	Height-Caliper Ratio	Survival in 1944	Mean Height Increment*	
						All Trees	Best 10 Per Cent of Trees
		(inches)	(inches)	(percentage)	(percentage)	(feet)	(feet)
1	1941—Ohio	4- 8	2/20	60	64.6	3.6	5.6
		8-12	2/20	100	70.2	2.8	5.3
		4- 8	3/20	27	72.9	3.7	6.2
		8-12	3/20	44	74.3	3.6	6.3
2	1939—Indiana	4- 7	2/20	45	80.2	6.4	8.7
		4- 7	3/20	20	83.6	6.7	9.6
		7-10	2/20	75	91.7	6.9	9.5
		4- 7	4/20	11	94.5	7.8	10.0
		7-10	3/20	33	95.1	7.5	9.8
		7-10	4/20	19	98.2	8.1	10.8
3	1939—Missouri	8-12	2/20	100	42.5	5.1	7.3
		4- 8	2/20	60	49.9	5.1	7.1
		4- 8	3/20	27	54.3	5.1	7.5
		4- 8	4/20	15	68.0	5.7	8.0
		8-12	3/20	44	70.0	5.5	8.1
		8-12	4/20	25	77.8	5.6	8.1
4	1940—Missouri	4- 7	2/20	50	70.5	3.3	4.8
		7-10	2/20	85	85.6	3.8	5.7
		4- 7	3/20	24	86.9	4.1	5.9
		7-10	3/20	38	93.5	4.3	6.3
5	1941—Missouri	8-12	2/20	100	57.0	1.6	3.4
		4- 8	2/20	60	58.2	1.9	3.4
		8-12	3/20	44	61.0	1.9	3.9
		4- 8	3/20	27	69.7	2.2	4.0
		8-12	4/20	25	76.2	2.3	4.4
		4- 8	4/20	15	88.0	2.6	4.5
6	1941—Arkansas	4- 7	2/20	50	79.2	2.1	4.9
		10-13	3/20	51	80.6	2.1	4.7
		7-10	2/20	85	81.9	2.2	4.8
		7-10	4/20	21	82.6	2.8	4.1
		4- 7	3/20	24	83.3	2.6	4.7
		10-13	5/20	18	87.5	2.8	4.7
		7-10	3/20	38	88.2	2.6	4.8
		10-13	4/20	29	88.2	2.7	4.6
		4- 7	4/20	14	95.8	2.9	4.9

\* From date of planting through 1944.

earlier production of salable thinnings, or (4) accounts for greater volume in the final crop trees. Differences in early height growth that are too slight to affect ultimate stand development may have statistical significance, but are not sufficient alone for justifying grading.

#### CALIPER AND HEIGHT CLASSES RELATED TO SURVIVAL AND GROWTH

In Table 1, the stock grades, made up of height and caliper classes, are arranged within each experimental planting in ascending order of survival percentages (Column 6). It is noteworthy that the data, so arranged, show that height increment tends to parallel survival rate. Evidently, grades of stock which show a high survival also make better-than-average height growth. This similarity of response strengthens the validity of the grading system as a means of predicting field performance of planting stock.

Certain inconsistencies appear in the data. Statistical analysis indicates that the relationship between stem caliper and survival and between stem caliper and height increment are, in all cases, statistically as well as practically significant. Seedlings in the lowest caliper class, the 2/20-inch, showed the poorest survival in practically all cases. Stem height, on the other hand, does not appear to be so closely associated with either survival or height increment. Only in Plots 2 and 3 was there a significant positive correlation between these variables. Plot 5 shows inverse relationships between seedling height and survival and between seedling height and height increment. Lack of more consistent relationships between height and survival and between height and height increment might be explained by the relatively low ground cover on the planting sites used in this study. In higher covers, which overtop the shorter but not the taller seedlings, field examinations show that the taller seedlings have the advantage in both survival and height increment.

The present study shows that stem diameter is a relatively good indicator of survival and height increment, but that seedling height alone is a questionable criterion to use in grading 1-0 shortleaf pine seedlings for field planting on sites of low ground cover.

#### HEIGHT-CALIPER RATIOS RELATED TO SURVIVAL AND GROWTH

Although not foolproof, the height-caliper ratio is a useful indicator of seedling sturdiness. In general, tall spindling seedlings having a high height-caliper ratio are less likely to survive and make satisfactory growth than sturdy seedlings of lower ratio. The 8- to 12-inch height, 2/20-inch caliper stock used on Plot 5 is an example of poor planting stock. On this particular plot height-caliper ratios decrease consistently with increasing survival and height growth. On the other plots lower ratios are generally, although not always, associated with better survival percentages and height growth. This is not always so, however, because seedlings may be too small or too large for field planting. In Plot 2 the stock having the poorest survival and height growth had a relatively low, usually favorable ratio of 45. The stock was too small for better results. Again, in Plot 6 the 10- to 13-inch, 5/20-inch stock had an

extremely low ratio and an acceptable survival. This stock was too large for high-quality planting with the mattock. Accordingly, if ratio alone is used, a range of seedling calipers and top lengths should be specified. In actual practice a simple range of top lengths for a given caliper or range of calipers is preferable. These two measurements can be quickly made at the nursery. In combination they are another way of expressing ratio without calculating it.

Since seedling height, caliper, and height-caliper ratios are significantly correlated with survival and height increment of planted seedlings, these characteristics can be used as a basis of grading nursery stock. In establishing usable grades, the minimum and maximum acceptable seedling qualities must be defined, and the intervening range subdivided into grades.

Study of the data in Table 1 indicates that planting stock should caliper at least 3/20-inch. Since few seedlings less than seven inches in height have a caliper as great as 3/20-inch, it is believed that 6- to 7-inch minimum height should be set. The maximum limits of caliper and top length are not so well defined, but seedlings with tops longer than 12 inches and with calipers greater than 4/20-inch do not appear to have any advantage in either survival or growth rate. Furthermore, when stock is larger than this, slower methods of planting must be used. Seedlings having calipers of 5/20-inch and larger are often short-stemmed and stocky. Ordinarily they can be planted successfully unless they have massive, bunchy, fibrous root systems that are difficult to plant in good contact with the soil. In dry years the mortality of this kind of seedling is frequently high. Stock grades, therefore, for general field planting should include only seedlings with calipers between 3/20 and 5/20-inch and top lengths of 6 to 12 inches. In observing these tops, the lower caliper of the range should be kept associated with the shorter tops, and the greater calipers with the taller tops. By this procedure spindly seedlings with high top-caliper ratios can be avoided. The degree to which grades of planting stock should be still further refined will depend upon cost of sorting and the increase in survival and growth of seedlings. The administrator of each forest area and the nurseryman supplying its planting stock will have to determine if further refinements are justified.

As previously pointed out, seedling height growth is directly correlated with survival rate. Statistically the relation is significant for most plots, but practically it is too soon to evaluate fully the differences in growth response. However, stock with higher growth rates appear to have certain advantages. It is better able to survive in competition with vegetation and to endure late summer drouths. For these reasons alone, greater attention to grades is warranted. Whether trees from the faster-growing grades will reach merchantability sooner, and be of higher quality than those from the poorer grades is uncertain; but after seven years, grade differences are still apparent.

On the assumption that 10 per cent of the planted trees are likely to remain as crop trees, the average growth of the tallest 10 per cent of the seedlings was determined for each grade in each of the plots. These

data are given in Table 1, Column 8. In Plot 6, no significant relationship between height growth and grade of planting stock is apparent. In the other five plots a definite relationship is seen. It is questionable whether in Plot 2 the difference of 2-3 feet in height in five years between the best 10 per cent and the average for all trees is important enough to serve as the basis for any conclusion.

The use of premium grade seedlings to establish a planted stand of more uniformly growing trees has been questioned. One argument in favor of planting nursery-run stock rather than graded seedlings is that more pronounced differentiation of crowns will develop. Such differences in growth will insure a sufficient number of final crop trees which will assume early dominance, and thereby necessitate less cultural work than if superior stock were planted; in other words, natural thinning is more likely to occur. On the other hand, the planting of

TABLE 2  
PROPORTION OF FIVE LOTS OF 1-0 SHORLEAF PINE SEEDLINGS FALLING IN THE SEVERAL  
HEIGHT-CALIPER CLASSES

Nur- sery	Year	Seedling Density	Height Class	Caliper Class					Total
				1/20- Inch	2/20- Inch	3/20- Inch	4/20- Inch	5/20- Inch	
		(number per sq. ft.)	(inches)	%	%	%	%	%	%
A....	1940	40	0- 4	22.2	17.3	0.0	0.0	0.0	39.5
			4- 8	1.8	28.3	11.8	.1	.0	45.3
			8-12	.2	5.6	9.0	.4	.0	15.2
			12 plus	.0	.0	.0	.0	.0	.0
			Total	27.2	51.2	20.8	.8	.0	100.0
A....	1939	35	0- 4	12.2	9.7	0.0	0.0	0.0	21.9
			4- 7	6.7	47.7	13.1	1.3	.0	68.8
			7-10	.0	2.1	3.2	1.4	.0	6.7
			10 plus	.0	.0	.6	2.0	.0	2.6
			Total	18.9	59.5	16.9	4.7	.0	100.0
B....	1940	30	0- 4	24.5	11.2	0.0	0.0	0.0	35.7
			4- 7	4.2	43.5	6.5	.0	.0	54.2
			7-10	.0	6.0	4.1	.0	.0	10.1
			10 plus	.0	.0	.0	.0	.0	.0
			Total	28.7	60.7	10.6	.0	.0	100.0
C....	1941	18	0- 4	9.5	7.2	0.0	0.0	0.0	16.7
			4- 7	4.2	21.7	10.3	3.6	.0	39.8
			7-10	.0	4.6	24.1	9.5	.5	38.7
			10 plus	.0	.0	.3	2.4	2.1	4.8
			Total	13.7	33.5	34.7	15.5	2.6	100.0
C....	1940	55	0- 4	16.0	6.2	0.0	0.0	0.0	22.2
			4- 8	3.5	49.4	7.2	.0	.0	60.1
			8-12	.0	5.4	8.6	3.3	.0	17.3
			12 plus	.0	.0	.0	.0	.4	.4
			Total	19.5	61.0	15.8	3.3	.4	100.0

graded seedlings requires fewer trees per acre to insure an early marketing of thinnings and a prompt start on liquidation of the capital investment.

#### STOCK GRADES IN NURSERY PRODUCTION

Table 2 shows for three different nurseries the distribution of seedling stock among the stem-height and caliper classes previously discussed. Although all lots of stock represented were from the same nurseries as those used in the field grade tests, they do not fully correspond in years of production. Table 3 groups the percentages shown in Table 2 into three stock grades defined as follows: (1) cull stock, made up of seedlings less than four inches high or less than 2/20-inch in caliper; (2) minimum acceptable stock, made up of seedlings having a height of four inches or more and a caliper of 2/20-inch; and (3) premium stock having a height of four inches or more and a caliper of 3/20-inch or more.

Most planters consider cull stock to be unsuited for field use. The minimum acceptable stock did not show up very well in field tests (Table 1) and is the minimum quality recommended for adverse planting sites. Premium stock is, of course, the cream of nursery production and capable of good field performance on any planting site in this region.

Table 3 shows that in the nurseries tested 22 per cent of the stock fell in the "premium class," 43 per cent in the "minimum acceptable" class, and 35 per cent in the "cull class." Until further refinements are made in nursery production methods or until cost of producing nursery stock is reduced, these three broad grades of stock may be all that can be justified.

The small proportion of premium stock is somewhat discouraging. Four of the five individual lots showed only about one-fifth of the seedlings classed as premium. In one case the proportion was as low as

TABLE 3  
PROPORTION OF FIVE LOTS OF 1-0 SHORLEAF PINE SEEDLINGS FALLING INTO THREE BROAD STOCK GRADES

Nursery	Year	Seedling Density	Broad Stock Grade		
			Cull Stock	Minimum Acceptable Stock	Premium Stock
		(Number per sq. ft.)	(Percentage)	(Percentage)	(Percentage)
A. . . . .	1940	40	44.5	33.9	21.6
A. . . . .	1939	35	28.6	49.8	21.6
B. . . . .	1940	30	39.9	19.5	10.6
C. . . . .	1941	18	20.9	26.3	52.8
C. . . . .	1940	55	25.7	54.8	19.5
Average . . . . .	....	..	34.9	43.1	22.0

one-tenth. During drouth years, especially, premium stock is superior in performance to the poorer stock. Since drouth years cannot be predicted at the time stock is selected and planted, high-grade seedling stock serves as survival insurance.

The minimum acceptable stock grade shows the highest proportion in all lots but one. Seedlings in this category may give excellent survival and acceptable growth on good sites in years of plentiful and well-distributed rainfall. Under other conditions failures or partial failures can be expected. Rainfall was exceptionally favorable to survival and growth on Plots 2 and 6 (Table 1), although the sites were poor. Even then, differences of 18 per cent and 16.6 per cent obtained between the minimum acceptable and premium grades. The quantity of this "minimum acceptable" stock is much out of proportion to that required for areas of good planting sites at present and therefore should be reduced by improved nursery practices.

The cull stock in the five lots ranged from 20.9 per cent to 44.5 per cent, with a mean of 34.9 per cent for all. These seedlings should be destroyed.

Under proper nursery conditions the proportion of premium stock could be materially increased. During the past ten years experience and research have greatly improved the average quality of shortleaf pine planting stock in the Central States. Further nursery investigations are needed to increase appreciably the proportion of the premium grade. These investigations include: (1) the determination of optimum seedbed density and methods to control it, and (2) the determination of soil conditions most favorable to growth and how to maintain them. Nurserymen agree that density is an important factor in producing superior stock and that a density of 20 to 25 seedlings per square foot should not be exceeded. During and immediately after germination, shortleaf pine seedlings cannot survive in soils with 500 parts per million of calcium and with pH values greater than 6.5 (1). Exploratory research has been conducted on responses of shortleaf pine seedlings in nursery beds: (1) to most of the various forms of mineral elements essential to growth and (2) to applications of acid peat (2). This research indicates that seedling development can be effectively controlled, and points definitely to the need for further investigations on most effective methods of control.

#### SUMMARY

In the springs of 1939, 1940, and 1941, grades of 1-0 shortleaf pine seedlings were planted in poorer-than-average old-field soils. These experimental plantings were made in Arkansas, Missouri, Indiana, and Ohio with stock from three Forest Service nurseries. Seedlings of the various caliper and height classes were planted in Latin Squares, each square being a complete design for testing the stock obtained from each nursery each year. Especially significant in the group of experiments was the fact that caliper and height classes were related to survival and growth.

In the range of seedling lots tested, the lower height-caliper ratios were associated with the better survival and growth rates. Calipers of 2/20-, 3/20-, 4/20-, and 5/20-inch and top height from 4 to 13 inches were involved. The best grades had heights from 6 to 10 inches and calipers of 3/20- and 4/20-inch, although seedlings with somewhat longer stems and with the larger 5/20-inch caliper gave good results. The largest stock was more difficult to plant which was perhaps responsible for its lower survival. It had either the larger calipers combined with the longer stems, or the larger calipers with the shorter stems of open-grown seedlings having massive roots.

In plantation establishment, survival capacity is considered a more important quality of seedlings than height growth capacity, and therefore should be given more weight in grade determination. Fortunately, better growth generally parallels better survival.

Caliper is a more effective criterion of survival and growth than stem height.

Nursery-run stock at the three nurseries was examined to determine proportions of the recognized grades found in each. Nearly 35 per cent of this stock in all nurseries was in the cull grade. Forty-three per cent of this stock was in the "minimum acceptable" grade and 22 per cent was in the premium grade. These percentages indicate the need for better stock production.

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# CUMULATIVE TALLYING BROUGHT UP TO DATE

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The unique idea of tallying on a cumulative composite volume table was advanced by S. R. Gevorkiantz of this Station in 1941. The cumulative feature facilitated computing the volume of each species immediately while in the field. A good merchantable composite volume table would be better, he believed, than the many untested tables based upon species and local differences.

The idea was worked out further with John W. Macon and published (6) in the August, 1942, *Journal of Forestry* under the title, "Estimating Volume on the Spot." Technical Notes 203 and 241 of the Lake States Forest Experiment Station served to distribute the composite tables for cordwood (1), the Scribner rule and the International  $\frac{1}{4}$ -inch rule (5).

The idea was accepted quickly throughout the Lake States and is now in common use by most public forestry agencies and many lumber and pulp companies. It was tested out in most forest regions of the United States and has been accepted for use in several.

The purpose of this paper is to present a fairly complete statement of the use of the cumulative tally sheet in its latest form, together with correction factors for species, adjustments for various standards of utilization, and adaptation of its use for other than  $\frac{1}{5}$ -acre plots.

## REVISED CUMULATIVE $\frac{1}{5}$ -ACRE TALLY SHEET

The tally form is divided into blocks, each representing a given d.b.h., bolt height class. A cumulative series of numbers is provided in each block. These numbers are volume units corresponding to the size of trees, indicated by the block, and multiplied by the proper factor to convert volume to the acre basis. In use, each tree on a  $\frac{1}{5}$ -acre plot is recorded in the proper block by crossing out consecutive numbers, *always beginning with the first number in the block.*

Last year the writer redesigned the tally sheet as shown in Figure 1 so that a legend need be used only when more than four species occur in the same diameter class. Species should be tallied in order of predominance. The revised form also provides for summarization by species.

In Figure 1, note that five white ash (WA) were tallied in the 6-inch class. Adding the last number crossed out to the right in each block (2 plus 4) we get 6, which is entered under totals per acre. Summarizing for pole timber trees we get a total of 14 for white ash and 22 for all

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<sup>1</sup>Maintained by the United States Department of Agriculture, Forest Service, in cooperation with the University of Minnesota at University Farm, St. Paul 1, Minnesota.

species. Pointing off one place to the left we get the volume of 2.2 cords per acre.

In the lower portion of the form, space is provided for tallying saw-timber trees and determining their volume per acre in board feet, International  $\frac{1}{4}$ -inch rule by the same procedure. In the example we find a gross volume of 79. Again pointing off one place to the left we obtain 7.9 M board feet per acre. Since an average defect of 15 per cent is indicated, the net volume shown near the center of the form is 6.7 M board feet.

Provision is made also on the form for tally of (1) trees in the 2- and 4-inch classes (upper left corner), (2) nonmerchantable (cull) trees (Column 3), and (3) mortality (trees which have died recently) (upper right corner).

Similar forms have been prepared giving cords and board feet by Scribner rule on the same sheet, and giving cords for all diameters on a sheet. Samples of these forms may be obtained from the Lake States Forest Experiment Station.

#### ADAPTATION FOR OTHER AREAS AND USES

The cumulative tally form may be used with satisfaction wherever the *average* form class for the trees is close to 78. In areas where the form class varies from this average, the volumes from the cumulative tally sheet should be adjusted by the following formula. Average form class minus 78 times 3 per cent equals  $\pm$  per cent correction needed. For example, if the average were 75:  $(75-78) \times 3 \text{ per cent} = -9 \text{ per cent}$ . Indicated volumes should be reduced by 9 per cent. Correction factors for individual species will be discussed later.

Ordinarily the sheet is used for tallying the merchantable trees on a  $\frac{1}{5}$ -acre plot (radius 52.7 feet) and the 2- and 4-inch trees on a  $\frac{1}{50}$ -acre plot (radius 16.6 feet). It is adaptable, however, to the tally of strips or blocks. If, for example, one wants a 100 per cent tally of a small wood lot, he makes the tally as usual but after summarizing the volumes and pointing off one place to the left, he should divide by 5 to convert to the volume of the entire area.

If one wishes to make a cut and leave cruise, he should tally all trees in the usual way but also record the cut (or the leave trees) by underlining the tally mark. If five numbers in a block were tallied and three were underlined, he would record the cumulative figure for all five as volume and for the first three numbers in the block as the recommended cut. Space is provided for summarizing the net recommended cut per acre on the form.

If there is a great deal more defect in some trees than in others so that an average defect factor is not applicable, the form allows for deduction of defect by species or diameter classes, or both as may be desired.

If a stand table is required, the number of marks for each species and diameter can easily be counted. Average volume per acre by species and diameter class may be read from the summary column. The Lake States Station has developed a method of determining growth for each



species and diameter in each type-size-density class which dovetails with the use of the cumulative tally form.

### COMMON ERRORS TO AVOID

As in the case of any tally by species, diameter, and height, considerable care must be taken to record trees by proper sizes. One must also be careful in reading the printed numbers.

Another common source of error is improper estimation of merchantable height. For example, the cordwood table is made for estimating to a merchantable top (minimum diameter of 4 inches inside bark). If

TABLE 1  
CORRECTION FACTORS FOR MERCHANTABLE HEIGHT

D.b.h. (inches)	Number of 8-foot bolts to 4-inch top* (percentage additional volume to 3-inch top)				
	2	3	4	5	6
6.....	23	16	12	.	..
7.....	17	12	10	8	..
8.....	..	10	8	6	5
9.....		8	6	5	4
10.....	..	..	5	4	3
11.....	.	..	4	3	3
12.....	.	.	4	3	2

\* Not to be used on trees where merchantability to 4-inch top is limited by defect or deformity. This table is taken from Technical Note No. 274 of the Lake States Forest Experiment Station (2).

utilization is to be made to a 3-inch top, the merchantable height should still be estimated to a minimum usable top of 4 inches and then be corrected by use of the Table 1:

Similarly, the tally of board feet must be based upon height to a merchantable sawlog top (minimum of 8 inches d.i.b.). Merchantable top may be defined as the point at which a limb diameter is equal to one-half the stem diameter, or above which no bolt would be 50 per cent sound. If utilization is to be made to a 6-inch minimum top,<sup>2</sup> the number of merchantable 8-foot bolts between the 8-inch and 6-inch tops should be tallied by species (and d.b.h. if desired). This might be called off as each tree is tallied and be recorded on the left margin. When the number of bolts is multiplied by 0.5 and the product rounded off to a whole number, the volume per acre in hundreds of board feet is obtained. This figure may be entered in the righthand column and summarized with other volumes.

### SPECIES CORRECTION FACTORS

When a volume table based on merchantable height rather than a

<sup>2</sup>In forest survey practice in the Lake States, aspen and softwood saw-timber volumes are estimated to a minimum top diameter of 6 inches d.i.b. and the other hardwoods to a minimum of 8 inches d.i.b. Softwood trees over 9 inches d.b.h. and hardwood trees (including aspen) over 11 inches d.b.h. are tallied as saw timber.

fixed top is used, the differences in volume between species becomes small. The use of one composite volume table weighed by the predominance of certain species then becomes practical. Furthermore, when net volumes are obtained on the basis of estimated cull deductions, the slight differences between species become even less significant.

According to our tests, the species differences usually compensate within a type composed of several species. What differences do occur are generally small and can be allowed for after field work has been completed. Table 2 presents the correction factors to be applied to *saw-timber volumes* obtained from the composite volume tables or cumulative tally sheet to get corrected volumes.

TABLE 2  
CORRECTION FACTORS FOR SAW-TIMBER VOLUME

Ash, black	.95	Hemlock	.92
green	1.00	Hickories	.98
white	1.00	Maple, red	1.05
Aspen	.93	sugar	1.00
Basswood	.98	Oak, bur	1.00
Beech	1.15	post	.93
Birch, paper	.93	red	.97
yellow	1.00	white	.97
Cedar, white	.90	Pine, jack	.90
Elm	1.05	red	1.04
Cottonwood	1.07	white	.96
Hackberry	1.00	Sycamore	1.07
		Walnut, black	.97

No correction of *cordwood volumes* is needed. Differences in unpeeled cordwood volume between species are very small. The loss in cubic-foot volume because of rapid taper is generally compensated for by the gain in cordage from looser piling. Thus, the rapidly tapering white cedar will show almost the same stacked cordage as spruce trees of the same size. Cedar will have less volume per stick but will require fewer sticks per cord. If cubic-foot volumes instead of cords were desired, corrections by species would be needed.

#### CONVERSION OF BOARD FEET TO CORDS

If one wishes to determine the volume in rough cords which is equivalent to the tally of saw timber by the International  $\frac{1}{4}$ -inch rule, he may use the conversion factors in Table 3. Multiply the number of hundreds of board feet on the tally form in a diameter class by the corresponding factor to obtain the tenths of cords per acre. For example, 8 (hundreds of board feet) in the 12-inch d.b.h. class is equivalent to 8 x 2.23 or 17 (tenths of cords) or 1.7 cords per acre.

If the tally has been taken on the International  $\frac{1}{4}$ -inch rule tally sheet and there is need to convert to Scribner (3) or to Doyle (4) volumes, converting factors are available in the Lake States Forest Experiment Station Technical Notes No. 283 and No. 287, respectively.

TABLE 3  
CONVERSION FACTORS FOR VOLUME IN ROUGH CORDS

D.b.h. class	Factor	D.b.h. class	Factor
	<i>Tenths of cords per hundred bd. ft. (or cords per M)</i>		<i>Tenths of cords per hundred bd. ft. (or cords per M)</i>
10	2.23	26	1.74
12	2.09	28	1.73
14	1.98	30	1.72
16	1.90	32	1.70
18	1.85	34	1.69
20	1.81	36	1.68
22	1.78	38	1.67
24	1.76	40	1.66

#### VOLUME IN TOPS AND LIMBS AND IN "CULL" TREES

The sound wood volume of the tops and limbs of saw-timber trees and of "cull" or nonmerchantable trees is quite variable but can be determined approximately by factors presented in Table 4.

The sound wood volume of nonmerchantable trees may be determined by multiplying the number of such trees tallied in the d.b.h. class by the corresponding volume shown in the second column in Table 4. This will give the volume in tenths of cords per acre which is similar to other figures on tally sheet and should be pointed off one place to the left to obtain cords per acre.

In determining the sound wood volume of tops and limbs, one should first determine the average merchantable height of the stand to the nearest 16-foot log. This will indicate which columns of factors in Table 4 to use for softwoods and for hardwoods. These factors should then be applied to the International saw-timber volumes by species and d.b.h. classes on the tally sheet. Since tally sheet volumes are in hundreds of board feet per acre, the answer will be in tenths of cords per acre and have to be pointed off one place to the left to obtain cords per acre.

#### CONCLUSION

The presentation of various factors for adapting the cumulative  $\frac{1}{8}$ -acre tally sheet to meet different needs may discourage use by making the process look complicated. In actual practice, however, only a few of these factors will be used at one time. The cumulative tally form enables the farm forester to tell the farmer within a matter of minutes after the tally is completed, what volumes of merchantable timber should be cut or left, and what volumes of cull trees, tops, and limbs may be salvaged. This cannot be done as quickly with the same degree of accuracy by any other known method.

TABLE 4  
CONVERSION FACTORS FOR SOUND WOOD VOLUME OF NONMERCHANTABLE TREES AND  
OF TOPS AND LIMBS OF MERCHANTABLE TREES

D.b.h. class	Nonmerchantable trees*	Merchantable Trees (Tenths of cords per hundred bd. ft. Int. 1/4," or cords per thousand)					
		Upper stems of softwoods and aspen†			Tops and limbs of hardwoods‡		
		1-log §	2-log	3-log	1-log	2-log	3-log
6	1	..	..	..	..	..	..
8	3	..	..	..	..	..	..
10	7	.3	.1	..	2.3	1.6	..
12	11	.5	.2	..	2.2	1.5	..
14	16	.7	.3	.1	2.2	1.4	.7
16	22	1.0	.5	.1	2.2	1.3	.7
18	27	1.1	.6	.1	2.3	1.2	.7
20	34	1.8	.7	.1	2.3	1.1	.6
22	41	2.1	.8	.2	2.5	1.1	.6
24	48	2.2	.8	.3	2.7	1.1	.6
26	57	2.3	.9	.3	2.9	1.0	.6
28	66	2.1	.9	.4	3.1	1.1	.6
30	76	2.4	1.0	.4	3.4	1.1	.6
32	85		1.0	.4		1.1	.6
34	97		1.1	.5		1.2	.6
36	109		1.1	.5		1.3	.7
38	120			.6			.7
40	130			.6			.8

\* The sound volume in those deformed or defective trees of commercial species which contain a net volume of less than 10 per cent of their gross scale.

† The sound wood volume in the upper stems of softwood and aspen saw-timber trees between the usable top minimum of 6 inches and the usable top minimum of 4 inches d.b.h.

‡ The sound wood volume of tops and limbs of hardwood (except aspen) saw-timber trees between the usable top minimum of 8 inches and the usable top minimum of 4 inches d.b.h.

§ Average merchantable height to the nearest log.

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# LUMBER RECOVERY FROM "WOODS WASTE" LOGS

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In the past, loggers in the Pacific Northwest have often left behind them as much as 15,000 board feet per acre of inferior saw timber. This is more than the average stand of virgin timber contains in many parts of the country. Since 1941, however, high lumber prices have made it practical to "relog"; that is, go back over the same ground and take out material that was left at the first logging, perhaps only five or six years earlier.

Several different sorts of material are obtained by relogging. There are large unsound trees, dead and down trees, and standing snags of the preferred species, Douglas-fir. There are broken chunks shorter than the customary log lengths but long enough to make standard lumber. In some areas trees of second-choice species, such as Western hemlock and white fir, form a large part of the relogged material. And finally there are trees of small sawlog size in all local species, trees that have been knocked down or broken or badly damaged in logging operations.

The forester favors relogging because it brings more complete utilization and leaves the forest in better condition. The lumberman favors relogging because it prolongs the life of his operation. But lumbering is a business proposition, and relogging will be continued only as long as it pays, which is a matter of costs on one hand and of selling prices on the other. This raises a question that is always with us in good times or bad, namely, what is the poorest log that can be sawed at a profit? Recent Forest Service studies shed some light on this question.

In the fall of 1947, the Pacific Northwest Forest Experiment Station shipped to the Forest Products Laboratory from southwestern Oregon a carload of "woods waste" logs. This means logs from material that was left in the woods because the operator doubted that it could be milled profitably. The material consisted of unsound logs, knotty top logs, small tree logs, and logs from broken chunks. The species were Douglas-fir, Western hemlock, white fir, Western redcedar, and incense-cedar. All logs were 8 feet long, and the total for all species amounted to 7,000 board feet. The primary purpose of the shipment was chemical utilization. First, however, the logs were sawed into lumber of standard size.

## OBJECT AND SCOPE OF TEST

The object of this work was to determine how much lumber and what qualities could be sawed from the woods waste logs. It is in no

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<sup>1</sup>Maintained at Madison, Wisconsin, in cooperation with the University of Wisconsin.

sense a detailed cost study. It does not give a direct answer to the question of which logs can be milled profitably. Rather, the study gives information which the lumberman can combine with his own knowledge of current costs and prices to arrive at the answer.

Although the woods waste material included five different species, this paper is confined to the chief one only, Douglas-fir.

## GENERAL PROCEDURE

### SCALING

The Scribner scale was used rather than the official Forest Service scale, the Scribner Decimal C. The Scribner scale reflects the board-foot contents of short, small logs more accurately than the other.

### SAWING

A 60-inch inserted-tooth circular saw taking a  $\frac{1}{4}$ -inch saw kerf was used. Thicknesses for merchantable lumber were 1 inch full and 2 inches full. Pieces down to 1 by 3 inches by 8 feet or 1 by 4 inches by 6 feet were saved and (except for the 3-inch size) even-inch widths were made. It was the practice to saw thin slabs so as to leave a face 4 to 6 inches wide for the first board. Cull lumber from unsound logs was largely sawed into 4 by 4's, the largest size which the Laboratory chipper will handle.

### GRADING

All grading was done in the rough green state, and West Coast Lumbermen's Association rules were followed. The logs had been lying around a year or more before shipment and some of them had season checks that extended through the slab into the first board. Checks were disregarded in grading, because they can be avoided and would be avoided to a large degree if anyone were making a serious attempt to mill such logs commercially. With this exception the grading rules were followed literally.

For the purpose of this report anything below No. 3 common in  $\frac{4}{4}$  or No. 2 dimension in  $\frac{8}{4}$  was classed as low-grade and cull lumber. Better qualities are classed as merchantable.

### WEIGHING AND MEASURING

Four classes of material were weighed separately: logs, merchantable lumber, low-grade and cull lumber, and slabs and edgings. Where logs are practically uniform throughout in moisture content, weighing should be an almost ideal way of evaluating these products. If heartwood and sapwood vary widely in moisture content, however, weighing may give some misleading results.

Merchantable lumber, low-grade and cull lumber, and slabs and edgings were all measured for volume by piling them in a one-cord rack. The actual amount of wood in a cord will vary considerably according

to the size and form of the pieces. The 4/4 and 8/4 merchantable lumber were piled compactly without voids. The 4 by 4 cull lumber was piled just as compactly but has less wood per unit of volume because of the voids (due to honeycomb or peck) in the sticks themselves. The slabs and edgings were piled loosely, with numerous voids between sticks. To some degree these things are reflected in the weights.

#### UN SOUND DOUGLAS-FIR

This material consisted of twenty-three 8-foot logs from fifteen different trees. The logs varied from 11 to 28 inches in diameter inside bark and averaged 18 inches. Some form of unsoundness was found in all of them, usually white speck or honeycomb or a combination,<sup>2</sup> although spots and streaks of soft rot occurred in four logs. A few had knots on the surface in addition to unsoundness, but most of the larger logs had an outer shell of sound wood that was clear on at least two sides. All logs were taper-sawed into 4/4 lumber so as to get the maximum of sound material.

The lumber sawed from these twenty-three logs amounted to 38 per cent of the scale of sound logs of equal size. The yield, tree by tree,

TABLE 1  
AMOUNT OF MERCHANTABLE LUMBER OBTAINED FROM UNSOUND DOUGLAS-FIR LOGS

Tree Number	Diameter Inside Bark, Small End (inches)	Number of 8-Foot Logs	Lumber Yield (board feet)	Log Scale* (board feet)
1	19	2	55	260
2	17	1	90	93
3	27	2	112	565
4	12	1	0	40
5	16	1	49	79
7	19	1	91	120
8	11	2	31	73
10	17	1	16	93
11	22	2	190	356
12	22	2	159	356
13	19	1	27	120
14	11	2	72	73
15	15	1	45	71
16	15	3	89	243
17	25	1	0	229
Total		23	1,056	2,771

\*Sound logs of equal size.

<sup>2</sup>Much of the Douglas-fir timber in southwestern Oregon is mature or over-mature, and consequently unsoundness is quite common there. The chief cause is the fungus *Fomes pini*. White speck is a very descriptive name that is applied to one type of unsoundness that is caused by this fungus. White speck varies considerably in degree, and often there is no clearcut dividing line between it and honeycomb, which is a more advanced stage of decay.

is shown in Table 1. Two of the trees, numbers 4 and 17, were very unsound and yielded no merchantable lumber. At the other extreme, trees numbers 2 and 14 yielded about as much as sound logs of equal size. This is quite possible in spite of their unsoundness, because the No. 2 common grade admits limited white specks and firm heart stain, while No. 3 common admits firm honeycomb and scattered spots and streaks of decay. The volume of the lumber yield, therefore, does not necessarily mean much unless it is tied into grades.

Table 2 shows the grades obtained. The defect that determined the

TABLE 2  
GRADES OF LUMBER OBTAINED FROM UNSOUND DOUGLAS-FIR LOGS

Tree Number	1/4 finish			4/4 common boards				Grand total
	B and better	C	Total	No. 1 Common	No. 2 Common	No. 3 Common	Total	
	(bd. ft.)	(bd. ft.)	(bd. ft.)	(bd. ft.)	(bd. ft.)	(bd. ft.)	(bd. ft.)	
1. . . .	0	3	3	0	0	52	52	55
2. . . .	0	4	4	28	23	35	86	90
3. . . . .	43	11	54	0	32	56	88	142
4. . . . .	0	0	0	0	0	0	0	0
5. . . . .	0	0	0	0	20	29	49	49
7. . . . .	25	19	44	19	0	28	47	91
8. . . . .	0	3	3	0	17	11	28	31
10. . . .	0	0	0	0	0	16	16	16
11. . . .	58	29	87	32	56	15	103	190
12. . . .	0	0	0	4	36	119	159	159
13. . . .	0	0	0	5	5	17	27	27
14. . . . .	0	0	0	8	35	29	72	72
15. . . .	0	0	0	5	40	0	45	45
16. . . . .	0	4	4	0	32	53	85	89
17. . . . .	0	0	0	0	0	0	0	0
Total . . .	126	73	199	101	296	460	857	1,056
Percent- age . . .	11.9	6.9	18.8	9.6	28.0	43.6	81.2	100

grade was usually some form of unsoundness or decay, although coarse knots and heart stain were factors occasionally. For the unsound logs as a group, the finish grades comprised 19 per cent of the lumber yield, and common grades of boards 81 per cent. But it is necessary to remember that the yield of low-grade and cull lumber was high and that only 38 per cent of the scale of sound logs of equal size was obtained in merchantable lumber. Logs from twelve of the seventeen trees had either a low lumber yield or a negligible amount of high grade lumber, or both. More than half of the common lumber was No. 3 common, which is ordinarily marginal.

The two trees with the highest lumber yields, Numbers 2 and 14, produced practically all common grade lumber, including more than one-third of No. 3 common.

The three trees that hold the most promise are Numbers 3, 7, and 11, the three which yielded nearly all of the finish grade lumber from

this entire group. These were medium to large trees as this material went, and had sound clear shells that gave a fairly good yield of finish lumber which normally sells for two to three times as much as the common grades.

According to Table 3, the low grade and cull lumber from this class of log amounted to nearly as much as the merchantable lumber on a weight basis, and slightly more on a cord basis. Loss in conversion on the weight basis was 23 per cent, largely sawdust, but including some chunks of bark and unsound wood.

TABLE 3  
WEIGHT AND VOLUME OF UNSOUND DOUGLAS-FIR MATERIAL

	Weight	Volume
	(pounds)	(cords)
Logs. . . . .	16,073	4.5 (375 cubic feet*)
Merchantable lumber. . . . .	4,768	1.2
Low-grade and cull lumber. . . . .	4,146	1.1
Slabs and edgings. . . . .	3,327	1.5
Loss in conversion. . . . .	3,712	.1 (9 per cent)
	or 23	
	per cent	

\* The cubic foot figure is for wood alone, no bark.

#### SOUND DOUGLAS-FIR

Sound Douglas-fir material consisted of forty-three 8-foot logs from twenty different trees. The diameter inside bark at the small end varied from 6 to 18 inches, and averaged 12 as compared with 18 inches for the unsound logs. Some of the logs were top logs from medium to large trees, others were butt logs from small trees, but nearly all showed knots on the surface. It was at once evident that most of these logs contained little if any finish grade lumber. Because of this and because Douglas-fir common grades are largely made into framing rather than into boards, a different sawing procedure was followed and 8/4 framing was cut as the chief product.

The sound logs produced no lumber of lower grade than No. 3 common boards or No. 2 dimension. Knots were nearly always the determining defect, and it was sometimes surprising how fast coarse surface knots decreased in size after a thin slab and one 4/4 board were removed. No. 1 framing required not less than four annual rings to the inch and a slope of grain not steeper than 1 in 10. A negligible amount was dropped one grade for failure to meet the ring requirements. A few logs showed spiral grain too steep to meet the slope-of-grain requirements, but none was too poor for No. 2 framing. Nearly all the knots were intergrown, of small to medium size, and consequently very little degrade would be expected because of loosening or dropping out of the knots in seasoning.

The amount of lumber obtained from the different trees is shown

TABLE 4  
AMOUNT OF MERCHANTABLE LUMBER OBTAINED FROM SOUND DOUGLAS-FIR LOGS

Tree Number	Top Diameter Inside Bark  (inches)	Number of 8-Foot Logs	Lumber Tally  (bd. ft.)	Log Scale  (bd. ft.)
101.....	16	1	60	79
102.....	11	1	27	33
104.....	10	1	27	27
105.....	13	1	55	19
106.....	9	4	99	120
107.....	11	4	156	179
108.....	10	1	28	27
109.....	10	1	16	27
110.....	13	3	191	177
111.....	10	2	71	60
112.....	14	7	652	667
113.....	11	3	126	122
114.....	18	1	29	107
115.....	6	2	21	20
116.....	9	1	21	20
117.....	9	1	19	20
118.....	9	1	21	20
119.....	16	1	20	79
120.....	8	3	60	63
121.....	10	2	67	60
Total.....			1,769	1,956

in Table 4. Logs numbers 114 and 119 had falling breaks which greatly reduced their lumber yield and put them in a different class from the rest. If these two logs are disregarded the sound logs produced lumber equal to 97 per cent of their log scale. If they are included, the yield drops to 90 per cent. In either case, the sound logs gave a much better return by volume than the unsound ones, as would be expected. The quality turned out to be almost entirely of sound common grade with no low-grade or cull lumber and relatively little high-grade material.

Details on the grades obtained are given in Table 5. The 6 per cent of finish grade lumber came very largely from one tree, Number 112. Seven 8-foot logs from this tree were shipped, and yielded 13.5 per cent of finish lumber. Two other trees, Numbers 109 and 111, gave good yields of finish material on a percentage basis, although the footage was small. Most of the trees, however, produced no finish lumber whatever. Four-quarter common boards, very largely No. 2 and better common, comprised 28 per cent of the yield. Framing formed two-thirds of the yield, and more than half of the framing was No. 1.

Table 6 shows nearly a 50 per cent recovery in merchantable lumber on a weight basis, as compared with 30 per cent for the unsound logs.

TABLE 5  
GRADES OF LUMBER OBTAINED FROM SOUND DOUGLASS-FIR LOGS

1, 1 finish				4 4 common boards				8 4 framing			
Log Number	B and better	C	Total	No. 1 Common	No. 2 Common	No. 3 Common	Total	No. 1	No. 2	Total	Grand Total
	(bd. ft.)	(bd. ft.)	(bd. ft.)	(bd. ft.)	(bd. ft.)	(bd. ft.)	(bd. ft.)	(bd. ft.)	(bd. ft.)	(bd. ft.)	(bd. ft.)
101.....	.	3	3	33	25	.	58	.	.	.	61
102.....	..	..	..	.	3	..	3	13	11	24	27
104.....	..	..	..	1	7	..	11	8	8	16	27
105.....	..	..	..	..	19	1	23	24	8	32	55
106.....	..	7	7	5	3	..	8	37	45	82	97
107.....	..	..	..	5	17	5	27	78	48	126	153
108.....	..	..	..	1	..	.	1	24	..	24	28
109.....	..	3	3	..	..	..	..	13	..	13	16
110.....	..	..	..	28	53	21	102	35	53	88	190
111.....	3	8	11	1	..	..	4	56	.	56	71
112.....	49	39	88	48	55	8	111	219	235	454	653
113.....	2	..	2	21	21	..	45	51	35	86	133
114.....	..	..	..	..	..	8	8	5	16	21	29
115.....	..	..	..	..	5	..	5	8	11	19	24
116.....	.	..	..	5	16	.	21	..	..	..	21
117.....	..	..	..	5	..	..	5	13	.	13	18
118.....	..	..	..	..	5	..	5	16	..	16	21
119.....	..	..	..	..	15	5	29	..	..	..	29
120.....	..	..	..	8	15	..	23	37	..	37	60
121.....	..	..	..	7	1	..	11	37	19	56	67
Total	54	60	114	177	266	51	491	674	489	1,163	1,771
Percentage	3	3	6	10	15	3	28	38	28	66	100



TABLE 6  
WEIGHT AND VOLUME OF SOUND DOUGLAS-FIR MATERIAL

	Weight	Volume
	(pounds)	(cords)
Logs.....	15,010	3.5 (319 cubic feet*)
Merchantable lumber.....	7,290	1.9
Low-grade and cull lumber.....	0	0
Slabs and edgings.....	1,195	1.5
Loss in conversion.....	3,325	.1 (3 per cent)
	or 21.5 per cent	

\*The cubic-foot figure is for wood alone, no bark.

### CONCLUSION

The wide range in the volume and quality of lumber obtained from the different woods waste logs strongly suggests that some of them might be milled at a profit.

## THE SMALL, LOW-INCOME LANDHOLDING: A PROBLEM IN FOREST CONSERVATION

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Small forest properties in private ownership are the crux of the problem of forest management in the United States. This fact stands out clearly in the findings of the recent Forest Reappraisal by the United States Forest Service. From the Reappraisal we learn that on properties smaller than 5,000 acres (which include three-fourths of all the private commercial forest land in the country), 71 per cent of the cutting is classed as poor or destructive. Only 4 per cent of the cutting on these small holdings follows good or high-order practices, as compared with 29 per cent on private properties of 50,000 acres or more, and 67 per cent on public forests.<sup>1</sup>

Within the class of private forest holdings smaller than 5,000 acres, the vast majority are very small properties. In fact, in the entire eastern United States, where most of these holdings occur, about 86 per cent are under 100 acres, and 70 per cent are under 50 acres. The problem of these very small properties has long been in the public eye. The six-tenths of them that are classed as farm woodlands have been the object of extensive educational and assistance efforts and the subject of a vast and ever-accumulating literature in forestry.

Anyone who works very long in the field of small-owner forestry becomes acutely conscious of the refractory nature of the problem. There seems to be a hard core of resistance into which it is extremely difficult for the forester to penetrate in his efforts to improve forest management. This hard core has been variously identified as the owner's "insufficient knowledge," "lack of interest," "poor bargaining position in the market," and so on.

The present paper deals with that particular hard core of resistance to forestry which is composed of *low income*. Relatively little attention has been given to low income as a factor in the small-owner forest problem. Yet studies made by the writer during the past decade in the eastern United States lead him to the conclusion that low income is the heart of the problem on at least a fourth of the small-owner forest land, and is intermittently a key factor on an even greater portion of our forests. Analysis suggests, indeed, that the small, low-income landholding is a special problem in forest conservation. To the extension forester and program administrator, the problem is difficult and challenging. No less is this true for the research worker, who may feel with some justice that

<sup>1</sup> United States Forest Service: The management status of forest lands in the United States. Report 3 from a reappraisal of the forest situation. 1946.

deeper knowledge of the problem is needed for its most effective solution. In this paper an effort will be made to describe the problem and then to suggest briefly some lines of pertinent research.

#### A CASE IN POINT

John Graham<sup>2</sup> is a farmer in Anson County, in the southern piedmont of North Carolina. His 70 acres of land yield him about \$200 a year in cash after farm expenses are paid. He and his family of four are hard put to make ends meet.

The Graham family took over this farm about twenty years ago. The land had already had 140 years of use. Originally it was part of a larger farm where tobacco and cotton were grown according to the exploitive methods brought inland from the old tidewater plantations. New ground was cleared each year to replace what had been depleted and eroded through heavy cropping. Today every part of the farm has been cleared, abandoned, and recleared at least three times. The Grahams' best 30 acres, now in fairly stable use for cotton, corn, and other field crops, consume nearly \$100 worth of fertilizer every year. Their poorest 30 acres is in woods, and more is being turned back to woods.

Little of value remains in the woodland. Once it was chiefly short-leaf and loblolly pines. Now oaks, hickories, and other hardwoods make up most of the thin stand of 27,000 board feet and 90 additional cords. The annual growth of 1,300 board feet and 6 cords is not even enough to put back what the family cuts for their fuel and other farm use, let alone to help furnish cash income.

In 1934, when a local itinerant sawmill operator offered the Grahams \$75 for their scattered saw timber, they were glad to get the cash. Twice during the war, when the pulp mills were reaching out for wood of very small size, the family cut and sold some pine—about \$140 worth altogether. In another few years, if left to grow, these trees would have been worth a great deal more. But the Grahams needed the money and could not wait. Now, even if they could forego opportunities to sell the very small amounts of new timber becoming merchantable from time to time, and even if they could keep the relatively worthless hardwoods from taking over the stand, it would be fifteen years before they could reap another substantial harvest for sale, and at least twice that before the forest capital would become large enough to be reasonably productive of yearly returns.

#### QUESTIONS UNANSWERED

What can the Graham family do to increase their income? What can they do to raise the value of their woodland? What can the public do to help them? Neither they nor the public have found an answer.

To this family, which needs income now, every day, the usual advice of the extension forester—to cut conservatively and let the trees grow—is

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<sup>2</sup> The name is fictitious. This and following examples, except where noted otherwise, are drawn from unpublished studies by the writer.

unacceptable. The timber management and marketing specialist cannot very well help them, for they have little or nothing to market. The bank will not lend them money on their woods in the absence of security.

And yet if this woodland could once be built up—and maintained—its productivity would help give the Grahams the money they need for a decent living and its timber would help to replete the flow of products for the community's needs.

Should the Grahams abandon their farm and look for employment where resources are better? Since 1940 a good many of their neighbors have done that, and the eroding fields are already spotted with young pine. Should the public help them find a place to go? The public then might acquire this land and manage it. Perhaps that is the only solution.

Or perhaps the Grahams themselves should acquire some of the neighboring abandoned land so as to increase their farm and woods holdings, reorganize their farming system, and bolster their income. They could be good stewards of the land if poverty did not force them into exploitation. Or perhaps there are other steps that they or the public could take to solve their income and forest problem without their abandoning the land.

#### A COMMON SITUATION

John Graham's situation is far from unique. Many other operators of small forest tracts face the same problem of low income, timber exhaustion, and inability to save or wait for capital to be replenished. In Graham's own county there are more than a thousand properties, operated by owners or tenants, similarly situated; and in North Carolina there are an estimated 100,000. The South as a whole has possibly about 680,000 such small, low-income landholdings; the United States, 1,300,000, with an average forest area of 50 acres. The number and acreage by region are estimated in Table 1. This 65.5 million acres is a great share of the nation's forest—a great share of its capacity to produce income and yield products for consumers—largely standing idle and lacking a specific program.

It is in the depressed, marginal rural areas of the United States, where natural and industrial resources are limited, that the chief con-

TABLE 1

<i>Region*</i>	<i>Number of small, low-income properties</i>	<i>Percentage of all private forest properties</i>	<i>Forest acreage in small, low-income properties</i>	<i>Percentage of all private commercial forest</i>
South . . . . .	680,000	41	40,800,000	21
North (& Central) . . . .	600,000	24	22 900,000	16
West . . . . .	20,000	17	1,800,000	5
United States . . . . .	1,300,000	31	65,500,000	19

\* Regions are those of the United States Forest Service Reappraisal. See report cited previously.

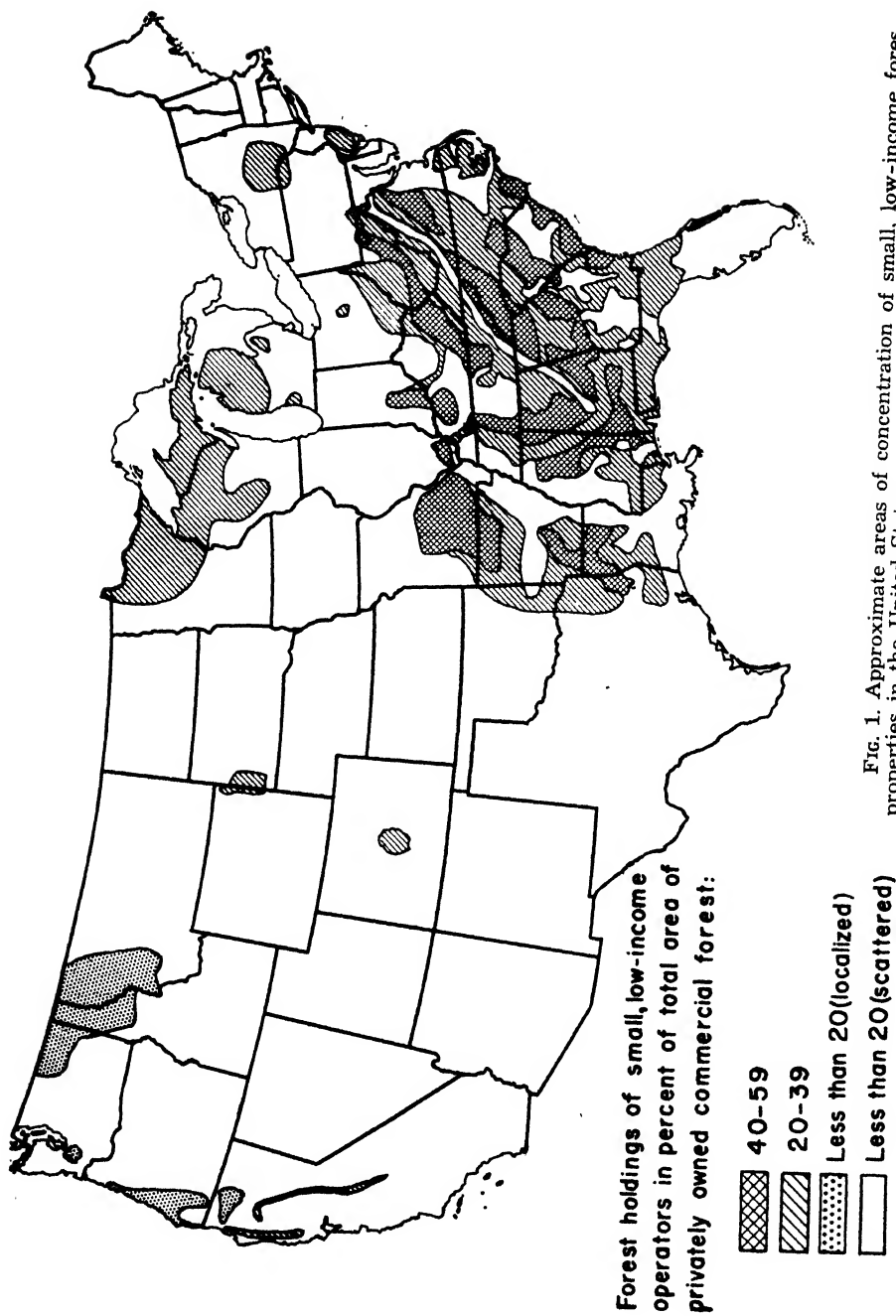


FIG. 1. Approximate areas of concentration of small, low-income forest properties in the United States.

centrations of small, low-income properties occur. The piedmont and coastal plains of the South—heavily populated, chronically depressed, under-industrialized, stripped of their best soil—comprise one large region of concentration. Another is the central and southern highlands: the Appalachians, Ozarks, and hills of southern Ohio, Indiana, and Illinois. Here rough topography, worn-down forests, and limited farming chances offer little to a congested population other than the necessity to exploit resources. A third region of concentration is the northern part of the Lake States. A fourth is the hills of the Pacific Northwest and northern California. In both these regions heavy lumbering on a wide scale has taken away the primary base of local prosperity and left mediocre land for farming and ranching.

Outside the great concentrations of small, low-income properties are such secondary areas as southern Colorado, the Black Hills, the pine barrens of New Jersey, and the Catskill section of New York. And beyond these again, scattered through even the most prosperous rural woodland areas, on the poorer soils or in otherwise unfavored spots, is many a small, low-income landholding.

The distribution of these properties and their acreage by region is about as shown in Table 2.

TABLE 2

<i>Region</i>	<i>Percentage of all small, low-income properties</i>	<i>Percentage of all small, low-income forest acreage</i>
South . . . . .	52	62
North (& Central) . . . . .	46	35
West . . . . .	2	3
United States . . . . .	100	100

#### AN APPALACHIAN AREA

In Breathitt County,<sup>3</sup> in the Appalachian Mountain section of eastern Kentucky is a dense, long-settled population which depends largely upon part-time, subsistence farming for a living. The land, however, is essentially nonagricultural: it is 70 per cent forest, and the only prime farming areas are the narrow ribbons of bottomland bordering the streams between the steep, sharp-ridged hills. The farms, clustered along these streams, produced in 1939 an average of less than \$300 worth of all products, most of which were consumed at home. Cash income, about \$200 per family, came mostly from off-farm work, including a little woods work, and from public allotments.

Not only farm resources, but all resources, are poor. Mining and industry are undeveloped. Cut over by large-scale operators many years

<sup>3</sup> William A. Duerr, John H. Bondurant, W. D. Nicholls, Howard W. Beers, R. O. Gustafson, and John B. Roberts: Farms and forests of eastern Kentucky in relation to population and income. Ky. Agric. Exp. Sta. Bull. 507. 1947.

ago and subsequently picked over for everything of value, the timber growing stock today amounts to only 1,700 board feet and 9 additional cords per acre, mostly beech and other unwanted species.

One 37,000-acre area typical of this region is held by about 300 private owners. Of these tracts, eight-tenths, containing 55 per cent of the forest, are in the small, low-income class. The typical small forest holding is less than 50 acres. In the eight years, 1937-44, nine-tenths of these low-income holdings yielded less than \$50 worth of products per year. Little of the return was in cash, and more than half of the owners made no sales at all during the period.

#### PROBLEM OF LOW INCOME

Breathitt County typifies the problem of low income that lies at the root of the difficulty of all small, needy operators. Low income, from the forest-management standpoint, is the problem of exhausted growing stock incapable of producing much timber return. From the community standpoint it is the general problem of depleted local resources and meager employment opportunities. Where resources are insufficient to give people an adequate living, the resulting pressure inevitably leads to exploitation.

In Breathitt County, where the pressure of population upon all resources is tremendous, no long-run plans can be made for any small forest tract, for tomorrow it may be cut heavily for whatever income it will yield, or it may be cleared in the constant quest for fresh agricultural soils. Even if all resources were built up to maximum productivity, the area could provide an average American livelihood to only one-third the people who live there today. Low income, underemployment, and overpopulation frequently are all symptoms of a single ailment.

Not low income alone, but low *cash* income, is the crux of the problem of the small, needy operator. Food and timber for subsistence, however ample, cannot satisfy more than a bare living standard. Somewhere, if only in the sale of a few scattered sticks of timber from an overworked woodland, cash must be found with which to enter the consumers' market. In Breathitt County, for example, the need is not to promote greater self-sufficiency, but to break down the barriers of physical and economic isolation. The people need to become a part of the general exchange economy, buying and selling products with the outside world. Forest products, preferably processed by an expanded local industry, are the County's natural trading stock. And if population pressure can be reduced, the necessary forests can be built.

#### TENURE PROBLEMS

In Breathitt County, as in many areas where small, low-income land-holdings are concentrated, unstable forest ownership and consequent lack of long-run interest on the part of owners is a problem. Nearly half of all properties changed hands in the ten years preceding 1944. Tenants,

too, shifted frequently, and this was significant because about three-fourths of all tenants had very wide latitude—approaching that of an owner—in timber cutting and management. In 1944, more than 80 per cent of all tenants had been in place five years or less.

Such shifting tenure of the land, inimical enough to any forest enterprise, is particularly damaging in the case of the small, low-income property. On such properties, typically, the forest capital will yield no substantial return for at least ten or fifteen years. The current forest value is little and is not, of itself, greatly worth protecting. Only the operator who anticipates reaping the future rewards for himself or safeguarding them for his family can be expected to take much interest in forest management now.<sup>4</sup>

On small, low-income landholdings operated by tenants rather than owners, the problem of disinterest, whether arising from brief occupancy or from other causes, is magnified. Few tenants take an owner's interest in building up the value of a property. Problems associated with tenant occupancy are most prevalent in the South.

#### A CUT-OVER AREA IN THE LAKE STATES

Northern Koochiching County, in the cut-over section of Minnesota, resembles much northern Lake States territory. Its level stretches of deep peat swamp are broken only by narrow strips of higher, alluvial land along the rivers. Settlement of this area came with the timber industry after 1900, to exploit the virgin spruce, tamarack, and pine.

After the timber had been worked over, many of the people stayed behind, and others soon joined them in the hope of founding a prosperous agricultural community. By the early 1920's, however, this hope was proven groundless and impossible of fulfillment on such barren lands. Families moved away; the costly ditches that were to have drained the swamps were abandoned; only thin lines of settlement along the rivers remained. Poor farm resources, depleted forest resources, low income, underemployment, tax delinquency, and a mounting public debt became the constant problems of the region.

In 1937, in a 213,000-acre area within this region, there were 240 resident families, of whom nine-tenths were small, low-income operators. The holdings of this low-income group made up about 30 per cent of all the privately-owned land in the area. A third of these small operators gained their entire livelihood from their own lands; most of the rest did comparatively little farming; intermittently they engaged in trucking or in woods work on adjacent state- and company-owned tracts. Gross income per family from all sources was about \$700.

The average family operated 120 acres of land. Of this, 80 acres was forest, cut-over and run down, three-fourths of it low-value aspen and brush, much of the remainder unmarketable hardwood. In all, the

<sup>4</sup> This is true because there is little or no recognized market for future forest values realizable under management, and what future values are reckoned in present market prices of property are discounted at a high rate.



sound timber volume averaged only 600 board feet and 6 additional cords per acre. With fuel wood for home use the chief harvest, the typical woodland yielded but \$70 worth of products annually, \$18 of this being cash from sales. Only 14 per cent of the operators cut any sawlogs in the five-year period 1933-37, and all of these were for home use.

#### PROBLEM OF FOREST CAPITAL

Northern Koochiching County offers an example of another of the major problems of the small, low-income property: the problem of depleted forest capital, need for putting capital into the forest, and difficulty of accumulating and retaining capital in the face of low income.

To build up forest growing stock takes an investment of labor, time, and money. Labor is needed for improvement work and perhaps planting. Time, or waiting, is needed to allow growth to take place. Money is needed for taxes, perhaps improvements such as fencing and planting stock, and most of all for tiding the operator over the waiting period. Labor is not, in most cases, a problem, but waiting and money are. A dollar now is worth more to the small low-income operator than several dollars a decade hence. With this high personal rate of discount, he is in a poor position to invest money in his forest enterprise or to wait for future returns.

#### NORTHERN CALIFORNIA HILLS

Along the western slopes of the Sierra Nevada mountains of California,<sup>5</sup> in a belt extending between the mountain timberlands at higher elevations and the wooded grasslands at lower elevations, are the upper foothills, a succession of rough ridges and deep canyons. This foothill belt was first generally settled in the gold rush after 1848. Subsequent invading and receding waves of mining, livestock ranching, lumbering, and crop agriculture have left a complex intermingling of cut-over, burned-over, second-growth pine; deforested lands in possession of hardwoods and chaparral; grassland, much of it brush-covered; and scattered patches of irrigated orchards and other cropland.

Most of this foothill land is owned by stock ranchers from the lower elevations and by nonresident individuals and companies holding or operating timber. Scattered throughout the belt, however, outside the areas of intensive settlement or farming, are small holdings of part-time subsistence farmers and rural residents. The great majority of these fall into the small, low-income class.

In 1933, in that part of the upper-foothill belt falling within the tier of six counties from Amador to Butte, about one-fifth of the total acreage of privately-owned commercial forest was in small, low-income landholdings. More than half of these holdings were smaller than 100 acres in total area; three-fourths of them were smaller than 200 acres.

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<sup>5</sup> David Weeks, A. E. Wieslander, H. R. Josephson, and C. L. Hill: Land utilization in the northern Sierra Nevada. The Giannini Foundation of Agricultural Economics. 1943.

On the average, about 40 per cent of the total tract acreage was second-growth pine timber; 30 per cent was hardwood woodland and chaparral; most of the remaining 30 per cent was grassland; cropland made up a very small percentage.

Most of the operators of these small, low-income properties received, in 1933, less than \$500 in gross cash income from all sources, including farm and forest products sold and outside employment in mining, road work, lumbering, and farming. Nearly three-tenths of the operators made gross cash incomes of less than \$100. Timber on the property provided almost no cash during the 1930's; timber was cut primarily for fuel and other home uses.

#### A VICIOUS CIRCLE

Timber depletion, coupled with small size of the forest holding, makes for low income. Low income leads to both a lack of interest in managing the woodland portion of the property and a need to get from the woods all of what little current return they will yield. These things, in turn, foster timber depletion. The problem of the small, low-income operator is to break this vicious circle and generate a new one wherein higher returns will lead to better management and a replenishment of capital.

In the northern California foothills, for example, a small-size forest tract is an inefficient management unit, and it is difficult to market profitably the small harvests from poorly stocked, immature second growth. From the operator's standpoint, the lands that warrant primary attention are his grazing lands and cropland. Indeed, one of the major forest problems is the repeated fires set by local people to improve and extend the range. The operator's indifference toward the effect of burning upon the forest illustrates how low income leads to disinterest, and this, in turn, to timber depletion. And the more depleted the woods, the lower the income.

#### A MIDWESTERN FARM AREA

Carver County, in southeastern Minnesota, is quite a different type of area. Small, low-income properties are to be found here, but only thinly scattered. Carver as a whole is one of the most prosperous rural counties in the state. Its level, fertile lands, its energetic and thrifty people, and its favored location near good markets place it high among the best areas in the Midwestern farming belt. In 1939 its farms produced an average of more than \$2,000 worth of products.

The virgin maple-basswood forests of the county were first extensively cleared by settlers after 1840, and by 1900 the present pattern of land use was essentially established: some 2,000 farms, averaging a little over 100 acres each, with residual scattered patches of woods occupying about a fifth of the farm area. Dairying has long been the chief farm enterprise; it provides the principal income of three-fourths of the farms, and nearly every farm has at least a few dairy

cattle. Ever since 1900 the county has had an average of about  $1\frac{1}{4}$  head of grazing livestock per acre of open pasture and hay land. Pressure upon the woods for forage has always been great, and has increased with the gradual depletion of open pastures. Today nine-tenths of the woodland is grazed.

Woodland grazing over the years has eliminated tree reproduction and allowed the stands to develop without an understory. Few stands contain trees smaller than 6 inches in diameter, and most of the timber is larger than 16 inches. Meanwhile steady though conservative cutting—mostly of selected trees for farm use—has gradually depleted this non-renewing resource. The average timber stand in 1939 was 2,300 board feet and  $7\frac{1}{2}$  additional cords per acre. Two-thirds of the stand area was very poorly stocked, with crown density less than 30 per cent, and 44 per cent of the area was so heavily grazed and thinned as to offer little or no possibility for forest management short of breaking and replanting the ground. Timber products harvested annually were valued at \$3.20 per acre of woods—about half of the potential harvest under management.

Depleted as the timber stands are, nevertheless in prosperous Carver County few properties fall in the small, low-income class: only about 4 per cent of the farms, containing 2 per cent of the woodland. These are mostly smaller farms, under 50 acres, often confined to the occasional tracts of poor land. Gross farm income is typically less than \$600, and often special circumstances make it difficult for the operator to supplement his income with off-farm work. More than half of the woods properties have no management possibilities in their present condition, and few of the remainder contain more than 5 acres of timber with definite management possibilities.

#### EFFECTS OF THE BUSINESS CYCLE

If a picture of Carver County a few years previously had been available, it would have shown a different situation, for in the years of deepest depression the proportion of holdings and of forest land in the small, low-income category was at least twice as high. So it is everywhere to a greater or less degree; in times of industrial and rural prosperity the problem of the small, low-income property shrinks to a minimum, but when industry and agriculture are depressed, the problem becomes most severe.

Historically, the problem of the small, needy operator reached its peak in the early 1930's, when depression, general timber exhaustion, and the fact that the nation had at last rather generally repudiated the ancient ideal of agrarian subsistence—all combined to create an unusually critical situation and to focus attention upon it. With a return of depression at some future time, however, the problem could again become at least as acute. The fact that today, in time of prosperity, nearly a third of all forest owners and a fifth of the private commercial forest fall into the low-income class is startling evidence of the seriousness of this ever-present problem.

Depression has varying effects upon the small, low-income landholding. In stable farming areas like Carver County, when farm income falls off, operators turn to every available means of earning a little cash. It is at this time that they are very apt to strip their woods if they can make a sale of timber.<sup>6</sup> In areas where subsistence and part-time farming and rural residence prevail, as in Breathitt County, Kentucky, depression brings a great return flow of people to the land, back from the industrial centers; and the pressure of population upon resources is increased.

In any case, depression deepens and spreads the two primary problems: low income and depleted timber.

#### NEEDED RESEARCH

The foregoing description of the small, low-income property and its problems may suggest in the reader's mind many possible lines of remedial action. It is not the purpose of this paper, however, to discuss action programs. The primary purpose has been to point out the problem. By way of conclusion, a few ideas will be suggested on the subject of needed research and the planning that flows from research, with the thought that a better understanding of fundamentals will help greatly to guide remedial action.

Basic to a consideration of needed research is the fact that the small, low-income property is not solely, or even largely, a forest problem. In most cases it is a problem also in sociology, farming, or industry, or indeed, a problem of the whole regional economy. In some cases the forest values are an almost negligible part of all the public and private values involved. Generally speaking, the problem is that of the rural slum, and emphasis is upon *slum*, and not upon rural or upon forest.

The rural slum differs from the urban chiefly in the greater susceptibility to exploitation of the rural environment. The Anson County tenant who chops up the woodlot for fuel and the Cook County tenement-dweller who chops up the banisters for the same purpose are responding to an identical need. It is merely easier for the former to accomplish his exploitation uncensured. Soil, water, and the wild growth of timber, edible seed, and game are there for him to draw upon in his extreme need. The presence of timber among the list is, in any particular case, largely fortuitous. Only as a secondary effect do small, low-income operators—whose problem is the result of maladjustment to the economic environment in general—create a problem of forest management and of the national timber supply.

So broad a problem calls for research on a broad front—primarily research along the lines of economics and sociology, and including forestry only as one of several fields for consideration. The approach to such research depends on the type of area in which the small, low-income properties are situated—or, rather, the type of fundamental maladjustment responsible for the problem. In general, two types of maladjustment may be distinguished, though the two are separated by a

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<sup>6</sup> It is recognized that in prosperous times, too, there is pressure to cut woodlands heavily, for then markets are good and buyers active.

broad and often indistinct line. These will be called, for convenience, primary and secondary maladjustments.

#### AREAS OF PRIMARY MALADJUSTMENT

The first, and more common, type of maladjustment is in the primary use of land over a considerable area—for example, its use for crops or pasture instead of forest. The typical area shows the following characteristics:

1. Generally very intensive use of land so that labor receives substandard rates of return.
2. Generally depleted land resources as a result of intensive use.
3. Underdeveloped industry and limited opportunities for development.
4. Overpopulation.

Here is a description of Breathitt County and many other Appalachian and Ozark communities. The description fits fairly well, also, a part of the piedmont and coastal South and numerous sizeable areas in the Lake States and the West. Altogether, such areas of primary maladjustment account for about six-tenths of the small, low-income properties in the United States.

For these areas of primary maladjustment, research is needed to evaluate broadly the income potentialities of the economy. What are the best uses of the land—as to kind of use and intensity of use? How many people will such use of the land directly support? What are the opportunities for industrial development based upon use of local resources including labor, and what are the prospects of employment from this source? What supplementary employment in trades and services may be expected if the potentialities of the economy are realized? What, in general, is the relation between population, resource use, and income in the area?

What adjustments may be needed in population if a reasonable optimum living is to be achieved? What adjustments are needed in land use, management practices, ownership, facilities for health and education? In some areas, attention may be directed at special problems of real-property taxation or tax delinquency or at matters related to land zoning. In other areas, special biological or engineering problems connected with building up the forests or other resources may need to be studied.

Finally, what is the attitude of the people toward such adjustments as may be indicated? If the need is for an exchange, rather than subsistence, economy, in which the emphasis would be not upon getting along with present resources, but upon seeking out or creating better resources, what is the people's attitude toward the changes that would be involved? How do they feel that such changes might be brought about?

The end result of such research should be to determine how general income may be raised so as to create an environment in which resource conservation, including good forest management, will be possible.

## AREAS OF SECONDARY MALADJUSTMENT

The second type of maladjustment is in the secondary use and the ownership pattern of land, especially over limited areas or on scattered holdings. This type is found in stable farming areas on farms that are too small for efficient operation or that need readjustment of crop, livestock, or woodland enterprises. It is found, too, in stable nonfarm rural areas, where adjustments are needed, not in population, but in type or conditions of employment. The typical area has these characteristics:

1. Misuse, or too intensive use, of individual, scattered landholdings.
2. Depleted resources and low income on scattered holdings.
3. Industrial development, actual or potential.
4. Community resources, actual or potential, sufficient to maintain the existing population at competitive rates of return.

In this class fall Carver County and most other stable farm areas. Much of the Northeastern States is included here, as well as parts of the Lake States, such as Koochiching County, and parts of the West and South. Such areas contain about four-tenths of the small, low-income properties.

In these areas of secondary maladjustment, research may well be directed principally at the organization of the individual landholding, with a view to defining needed adjustments in the size or management of the business, and in its use of land, capital, and labor.

What is the most efficient combination of land and capital with the labor available on individual holdings? What adjustments are indicated within the business, such as in ownership boundaries, land use, or type of forest or nonforest enterprises? Are forest enterprises likely to be the chief means of raising income, as is true in Koochiching County? Or are farm enterprises probably the main hope, as in Carver County? What use may be made of credit, and what credit facilities are accessible to the operator?

Analysis may disclose that there is little opportunity for consolidation of landholdings and that the possibilities for raising income through internal readjustments within the business are limited. In this event, attention turns to outside employment for labor. What returns might be expected from part-time operation of the business, coupled with industrial or outside forest work? What role may be played by nearby public forests in offering part-time employment? May additional processing of farm or forest products provide needed employment, and how may processing plants be successfully established?

Such research, like that in areas of primary maladjustment, has for its goal the raising of incomes—through the medium of all available resources including forests. The object is to remove the excessive pressure upon resources that lies at the root of the problem of the small, low-income landholding.



## FOREST PRODUCTS RESEARCH IN OREGON

PAUL M. DUNN

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Research in forest products for Oregon dates back to about 1927 when studies in the seasoning of certain native hardwoods were sponsored by the School of Forestry at Oregon State College. Two graduate students received the first Master's degrees in this type of work in 1928. The same year, Prof. T. J. Starker started his Post Farm experiment which during the following twenty years has resulted in the establishment of fifty-nine separate study plots of 25 fence posts each. The majority of the western timber species with a wide variety of preservative treatments and the corresponding checks were used. The results were published periodically and have been especially valuable and interesting to the farmers, and public and private agencies.

These investigations and studies in related engineering fields were carried on for about twelve years with increasing interest on the part of the college staff and industry. In 1940, the Department of Wood Products of the School of Forestry recommended the appointment of an advisory committee comprised of representatives of industry, and the creation of an Institute of Forest Products for the purpose of encouraging increased interest in better wood utilization and products research in Oregon.

A steady increase in the prominence of local forest industry and economy, emphasized by the fact that in 1938 Oregon became the leading state in the nation in respect to lumber production, was an important factor. Currently the forests contribute about 60 per cent of the income of the state, and there is no reason why the proportion should change greatly. As a result of this early work and activity, and the developed interest on the part of representatives of industry and the general public in more complete utilization of the timber resource, recommendations were made for specific legislative action in 1941.

### STATE SUPPORT

Early thought pointed mainly at the responsibility of the state to finance research projects, and the idea of a forest utilization experiment station at the College was suggested. However, the first measure provided for a biennial appropriation of \$25,000 to finance studies "to improve the utilization of present waste materials resulting from the harvesting of forest crops, the manufacture of lumber and other forest products." Provision was made for the establishment of the research program at Oregon State College, functioning through the State Board of Forestry in cooperation with the School of Forestry. The act set up an Advisory Committee for the program and outlined its functions, but there was no indi-



cation of permanence. Therefore, in 1943 the law was reworded to make the project continuous though dependent upon biennial legislative appropriations.

In 1945, the 1943 act was amended to establish the Forest Products Laboratory and to authorize the director, who is the dean of the School of Forestry, to accept funds from and to cooperate with individuals, corporations, associations and public agencies wherever and whenever advisable to further forest products research. It also granted authority to the State Board of Forestry to accept gifts of land and money from the United States of America or any of its agencies for the purposes of carrying on forest products research.

#### ADVISORY COMMITTEE

The law under which the Forest Products Laboratory operates provides for an Advisory Committee of eight, six of whom are appointed by the Governor. Each of the following agencies or groups recommends a member for appointment: West Coast Lumbermen's Association, the Willamette Valley Lumbermen's Association, the Western Pine Association, the School of Forestry at the State College, the Oregon Plywood Interests, and the Pacific Northwest Forest and Range Experiment Station. The Governor is ex-officio member of the Council and its chairman, and the State Forester is secretary. Members of the Council receive no compensation for their services, but are paid for actual traveling expenses incurred in attending Council meetings or for the performance of other services:

Functions of the Advisory Committee are:

1. To survey the entire field of research in wood utilization for the purpose of assembling definite information covering current research projects as well as past accomplishments and rendering practical counsel in the field of economic forest utilization.
2. To explore new fields for the utilization of forest products and to encourage the establishment of new industries of this type within the state.
3. To guide and approve all research activities undertaken by the Forest Products Laboratory.
4. Through contacts with wood-using industries to suggest promising wood utilization projects to other research organizations.
5. To recommend the compilation and release to industry and to the general public all research information and data.

#### FINANCES

During the first six years of the program's existence, the budgets were small. This limited the scope of activity. The biennial appropriations were: 1941—\$25,000; 1943—\$26,000; and 1945—\$48,370. Increased production of forest materials and the demand created by the war developed added interest in various utilization projects. The re-burning of the Tillamook area in 1945 emphasized a need for more thought toward the future of this very important resource. Considerable interest in chemical utilization of waste wood developed from the projected construction of the wood

sugar-alcohol plant in western Oregon. As a result, the 1947 Legislature appropriated \$100,000 for products research and also placed a "severance" tax of 5 cents on every thousand board feet of forest products harvested, to be effective for a period of six years. The income from this tax, which is estimated to bring in approximately \$300,000 annually, is divided, after the cost of collection by the State Tax Commission is deducted, 60 per cent for research by the Forest Products Laboratory and 40 per cent for forest management research by the State Board of Forestry. The funds available for products research during the current biennium therefore may approach \$420,000.

#### PHYSICAL FACILITIES

During the war years, many of the studies were carried on in the laboratories of the several cooperating college departments. However, two small buildings were erected adjacent to the School of Forestry dry kiln and housed the carbonization and fiber board projects. Increased interest throughout the state encouraged the State Board of Higher Education to place the construction of an industrial research building as item number one on its ten-year plan. This building was completed in July, 1947, at a cost of \$195,000, and approximately one-half of the space, 18,000 square feet, is allocated to the Forest Products Laboratory. This is a two-story lumber-steel-tile structure, 60 x 300 feet in dimension. The space is divided into 20 x 23 foot bays and the forestry portion is distributed as follows: *First floor*—dry kilns, 3 bays; plywood and fiberboard laboratory, wood preservation plant, and woodworking shop, 2 bays each; and timber testing laboratory, chemical utilization laboratory, controlled temperature-humidity chambers, and machine shop, 1 bay each. *Second floor*—offices, library, and storerooms, 5 bays; wood chemistry laboratory, 3 bays; physical laboratory, 2 bays; and wood technology laboratory, 1 bay. The charcoal retort and carbonization studies are confined for the time to the old building.

Considerable new equipment has been purchased and some was procured from war surplus, but many items are still on order or to be designed and assembled. Full use will be made of available laboratory equipment in cooperating departments and agencies, and it is expected that certain studies may be carried on at plants out in the state. However, the plan calls for the procurement of all the essential equipment necessary for the whole range of chemical and physical utilization projects, which will eventually provide a first-class research facility in Oregon.

#### STAFF

The staff also had a small beginning, starting with several of the college specialists on a part-time basis—namely men in the Wood Products, Chemistry, and Engineering departments. Soon a full-time wood technologist was employed, and now the number has grown to eight full-time men, several graduate assistants, and part-time specialists. While the Dean of the School of Forestry is officially the director, the current expan-

sion necessitated the appointment of a technical director, Dr. Phimister B. Proctor, who is in charge of the laboratory program. The other full-time men include a wood chemist, a chemical engineer, and five wood technologists, with another chemist and a wood technologist to be added. Also, a clerical staff and two mechanics are provided.

The personnel is divided into three main groups to conform to the nature of the projects: chemical utilization, wood technology, and industrial service. Each section has or will have one man in charge who is responsible to the technical director.

#### RESEARCH PROGRAM

The first study initiated in 1941 was a survey of the quantity and quality of waste at the sawmills in the State. (See "Inventory of Sawmill Waste in Oregon.") The data showed 46 per cent of the pine logs and 49 per cent of the fir logs left as waste at the mills, and a gross quantity of over one million units of material accumulating or being burned annually. Also, a ton of waste results from every 1,000 board feet of logs cut, and Oregon has been cutting from 5 billion to 7 billion feet annually. Certain studies dealing with the use of the material followed, and the current program is largely an expansion of the first projects. However, many associated ideas have been added.

Effort was directed toward the possible utilization of large amounts of the waste since sawdust, hogged wood, slabs, and edgings formed the bulk of the unused wood material. A study dealing with the transportation problems and costs of bulk material was completed. Chemical projects pointed toward the use of sawdust and hogged wood as fiberboard stock, as well as the use of the Douglas fir bark and its corky fibers, were undertaken. Carbonization of raw wood waste was investigated and a small retort was constructed. An associated study involving the possible use of the wood tars from the charcoal experiment followed. When the wood sugar plant to utilize wood waste was started, associated studies dealing with hogged wood storage, and the utilization of the byproducts of lignin, calcium sulphate, and waste liquor as sources of usable materials were initiated. Later studies covering the kinds and amounts of forest waste accumulating during the logging of the timber were started and the information gave encouragement to re-logging and salvage logging operations by industry. Other studies considered the unused timber species such as lodgepole pine and the native hardwoods. A total of twenty-five major publications and articles have been prepared covering the several projects completed or in progress.

The present program is outlined below by major phases of activity:

#### CHEMICAL UTILIZATION SECTION

##### A. Wood chemistry

1. Wax recovery from lignin residue of wood sugar-alcohol manufacture. Shows promise of reducing cost of alcohol by 20 cents per gallon and a patent application is being made.

2. Production of tannin from Douglas fir bark.
3. Analysis of chemical constituents of Douglas fir bark.
4. Chemical analysis of Ponderosa pine bark; cooperating with Western Pine Association.
5. Analysis of the chemical composition of the extractives of Douglas fir wood.
6. Chemical analysis of all western woods; cooperating with Oregon State College Chemistry department.
7. Chemical analysis of decayed wood.

B. Carbonization

1. Production of 5-ton sample of granular charcoal from Douglas fir sawdust for testing by the carborundum industry.
2. Design of a one-ton-per-day charcoal plant.
3. Analysis of tars from wood carbonization processes.

WOOD TECHNOLOGY SECTION

A. Fiberboard and related products—

1. Study of essential properties and ultimate production of speciality products from wood fiber.
2. Special surface treatments for hardpressed fiberboard.
3. Production of containers for agricultural products.
4. Cooperative projects with industrial organizations.

B. Plywood and laminated products—

1. Utilization of cedar tow in panel boards.
2. Utilization of No. 3 Common lumber in prefabricated panels; cooperating with West Coast Lumbermen's Association.
3. Development of molded products.
4. Development of a board with waste-material core and veneer surfaces.
5. Study of adhesives.
6. Utilization of decayed or defective wood as laminated core stock.
7. Study of operating factors associated with high frequency gluing.
8. Study of gluing characteristics of Oregon woods, chiefly hardwoods.

C. Seasoning—

1. Drying Oregon hardwoods.
2. Improvements in kiln design; especially small units.
3. Comprehensive study of drying factors of wood.
4. Testing of end sealers; cooperating with West Coast Lumbermen's Association.
5. Study of solvent seasoning; by arrangement with Western Pine Association.

**D. Wood preservation—**

1. Study of durability of various native Oregon woods as railroad crosstie material; cooperating with Southern Pacific Company. 1000 ties each of all species will be track tested.
2. Continuation of T. J. Starker Post Farm study.
3. Design of experimental treating plant.
4. Study of resin coated nails for measuring moisture content of wood.
5. Screening chemical compounds for fungicidal value; cooperating with Prevention of Deterioration Center, Washington, D. C.
6. Study of development of accelerated methods of treatment and controlling end penetration; cooperating with several agencies.

**E. Timber testing—**

1. Study of strength properties of low-valued Oregon species; especially hardwoods.
2. Development of small-scale test panels and correlation with full-scale material.

**F. Miscellaneous—**

1. Comprehensive study of amount, kind and rate of decay in old-growth Douglas fir; cooperating with various companies and agencies.
2. Study of use of wood sugar molasses and yeast as livestock feed supplements; cooperating with United States Forest Service and Oregon State College Agriculture Experiment Station.
3. Manufacture of box ends from white fir; cooperating with Wooden Box Institute.

**INDUSTRIAL SERVICE SECTION****A. Information—**

1. Editing, publication, and distribution of research data.

**B. Investigations—**

1. Survey of kind and number of sawmills by counties.
2. Utilization of No. 3 Common lumber; cooperating with West Coast Lumbermen's Association.
3. Grade and mill studies in connection with decay projects.
4. Contacts with wood-using and lumber plants in state.

**COOPERATION**

The policy of the Advisory Committee and Laboratory is to cooperate fully with all agencies, both public and private, within or outside of Oregon, in order to assemble, develop, and disseminate ideas or techniques of economic interest to organizations interested in the fuller utilization of the forest resource. Effort is stressed to minimize duplication of work on the various projects between agencies. Extensive cooperation has been

developed with the United States Forest Products Laboratory, Timber Engineering Company, the West Coast Lumbermen's Association, the Western Pine Association, the Bureau of Land Management (O & C Lands), the State of Washington, and private corporations such as: The Weyerhaeuser Timber Company, Simpson Logging Company, Fir-Tex Company and many others. Of special mention is the joint program with the Chapman Manufacturing Company of Corvallis, whereby the company is now manufacturing a hard fiberboard from Douglas fir slabwood.

Many contacts have been made with technical advice and service given to local lumber and logging concerns and organizations such as Chambers of Commerce in the various communities. The major objective of the whole program is to increase the utilization of forest products through development and encouragement of a fuller use of current saw-mill and woods waste, and unused timber species.



## GROWTH OF TREE PLANTINGS FOR EROSION CONTROL IN THE SOUTHEASTERN REGION

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During the past thirteen years about 180 million trees have been planted in the Southeast. These trees were planted as part of the intensified erosion control program conducted with the technical assistance of the Soil Conservation Service. Extensive plantings were made in erosion control demonstration projects and CCC camp areas and later by farmers in soil conservation districts.

These trees have been planted chiefly on private land in areas that, for the most part, had become so badly eroded they no longer could be used profitably and safely for crops and pasture. A wide range of site conditions are represented in these tree areas. As a general rule they are characterized by severe sheet and gully erosion, moderate to steep slopes, and low fertility. Soils derived from sandstone predominate but both calcareous and shale soils are represented. These lands have been used chiefly in the past for the production of cotton, corn, and tobacco and in parts of the region for grazing.

Generally the ground cover on most of these areas at the time of planting was light. In some places, however, it varied from nearly bare to heavy stands of broomsedge and similar grasses. There was very little woody growth on most of the areas. Such perennials as blackberry, sassafras, persimmon, sweet gum, and wild plum occurred on some of the sites, usually as individual plants or in small patches. Almost no clearing of existing vegetation was done prior to planting.

In some cases sites for tree planting were carefully prepared. Elaborate practices, including sloping and dynamiting of banks and construction of check dams, were applied to many gullies. Furrowing, ridging, and fertilizing were practiced on a small percentage of the fields planted. A few areas were cultivated for a year or two after planting. Considering the total area planted, however, a very small proportion was affected by this site preparation.

In the lower part of the region, particularly in the sandstone soils, most of the trees were planted with the use of the planting bar or dibble. In the sections of heavier soils as found in most parts of Kentucky and Tennessee, the common grub hoe was used.

In establishing most of the plantings a spacing of 6 x 6 feet was used. On some of the more critical areas, in both fields and gullies, the trees were spaced as close as 4 x 4 feet.



Pine was the species used in planting most of the areas. Loblolly, slash, and longleaf pine were planted in the southern part of the region and shortleaf, loblolly, white, Scotch, pitch, and Virginia pine in the northern part. Much black locust was used in the earlier plantings. This was particularly true in the limestone sections of Kentucky, Tennessee, and Virginia. A very small part of this planting included the use of such hardwood species as black walnut, tulip poplar, ash, and oak (usually red or white oak). Both pure and mixed plantings were made.

The major objective in this planting program was to reestablish ground cover on eroded land as quickly as possible to check runoff water and soil washing. Recognizing the necessity of returning a profit to the farmer while conserving his soil, the production of a wood crop of value was another major objective in the establishment of these tree plantings on farms. The establishment of cover for wildlife and recreational use also was considered.

The importance of protecting these young planted stands of trees from fire and grazing was emphasized in all agreements with the farm owners. In many cases fences were relocated and constructed to insure protection from grazing. The use of CCC labor afforded the farmer a great deal of assistance in protecting these areas from fire. Later, as the camps were closed, the farmer owners of these planted trees had to look elsewhere for this assistance—chiefly to State Forestry Departments through the farmers', local soil conservation district supervisors.

Follow-up studies of these plantings were started promptly by the Soil Conservation Service. The chief objectives of the studies were to check survival, rate of growth, establishment of ground cover, and to encourage cooperators to protect the areas. In making these studies, many plantings that were selected as representing common conditions, have been visited at periodic intervals of from one to three years. This has made it possible, in many cases, to follow rather closely the general development of the stands, the natural invasion of native plants, and the gradual accumulation of litter on the ground. Other interesting observations were also made which will be mentioned later in this report.

In making these studies the foresters have been materially assisted by agronomists, engineers, and soils specialists. A special effort has been made to include a soils specialist in this study in order to insure a more complete and accurate analysis of soil and site conditions.

Plantings covered by this study are located in all the states south of the Ohio River and east of the Mississippi River except West Virginia. They, naturally, involve a wide range of soil types and site conditions. Well over 150 plantings have been studied, many of them several times at periodic intervals. Included in this number are a few older plantings that had been made by individuals and public agencies. Observations and measurements of a large number of the plantings were recorded on a form provided for the purpose. These records were supplemented frequently by photographs, including many follow-up pictures from established photo stations.

The observations and measurements made in these tree planting

studies, extending over a period of about 13 years, are summarized in the following paragraphs and tables.

### 1. PROTECTION

The protection afforded these plantings varied considerably. Many areas were protected only for the five-year period specified in many of the earlier agreements made with cooperators. Many other areas were protected as long as the original fence remained an effective barrier to livestock. Very little fence maintenance was observed. Damage from grazing varied from negligible to virtual destruction of the planted trees. Serious soil compaction also resulted. The damage varied with the



FIG. 1. A seven-year-old pine planting severely browsed by cattle.

intensity of grazing and was much heavier in the northern part of the region than in the southern part where livestock are not as numerous on farms. Browsing of trees by livestock occurred on both pines and hardwoods. Despite the all too common belief that pine are not browsed, pine plantings were studied where the trees had been virtually destroyed by intensive browsing (Fig. 1). Complete protection from grazing was recorded in 86 plantings out of a total of 124 where records were made.

Evidence of fire was found in only seven plantings out of a total of 125 where this item was recorded. A rapidly increasing number of farmers in soil conservation districts are establishing and maintaining firebreaks as a very important practice in fire control.

### 2. SURVIVAL

While survival was usually adequate to provide a complete forest cover within ten years, there were plantings found with very thin

stands and others with spotty stands. Few replantings by cooperators to fill in the blanks were found. This brings out another reason for closer initial spacing at least until farmers become sufficiently interested to do replanting. The pine species survived far better than the black locust and other hardwoods. It was commonly observed in pine plantings that if the seedlings survived the first year they would generally persist even on the worst sites. As an example, survival counts in a planting of loblolly pine in Georgia on a very severely eroded and galled 1/16-



FIG. 2. Pine was planted on the left and black walnut on the right thirteen years ago.

acre plot were: 65 trees in 1940 (one year after planting), 63 in 1941, 63 in 1942, 62 in 1945, and 62 in 1947. By contrast, many areas planted to black locust showed a rapid reduction in percentage of survival over a period of several years. There were many eroded areas with pine and hardwoods planted side by side where the pine over the years gained in vigor and the hardwoods have gradually disappeared (Fig. 2). In order to establish a full, uniform stand of trees and a sufficient accumulation of ground cover as early as possible, this study stresses the importance of watching survival and replanting immediately after blanks occur.

### 3. NATURAL INVASION

Where plantings were protected from grazing and fire it was gratifying to note how promptly, under many conditions, native annual plants invade these eroded areas and how soon perennials, including the

woody species, follow. One of the most commonly found woody species invading these areas—even the more severely eroded—is red cedar (*Juniperus virginiana*). It is found generally all over the southeastern region invading these planted areas as a conspicuous member of the understory. This prompt natural invasion is particularly significant in the early establishment of ground cover when the planted trees are getting started.

There are areas under observation, however, where natural invasion



FIG. 3. Planting Tennessee 5 (Table 1) when it was thirteen years old. The surface of the ground was completely covered by pine litter here when the trees were between five and six years old.

of native plants has been negligible after ten or more years. Usually these are the more severely eroded areas and frequently small spots within such areas.

#### 4. ACCUMULATION OF GROUND COVER

The time required for the accumulation of enough litter to cover the ground completely was found rather variable. In some pine plantings a complete ground cover had become established in five to six years (Fig. 3). In other plantings on the less favorable sites a complete ground cover does not exist yet, thirteen years after the trees were planted. Obviously, survival and subsequent density of stand, along with natural invasion by native plants, are major factors in the development of ground



**FIG. 4. Tennessee series. (A)** Shortleaf pine five years old planted on sandy Coastal Plains material with the Loess cap all washed away. **(B)** Same planting when nine years old; average height about 7 feet. **(C)** Same planting when fourteen years old; average height about 11 feet.

cover. In many of the worst eroded areas, "galled" spots occur where frequently survival is lower and growth is slower than in the rest of the area. Frequent examples of this condition were encountered in western Tennessee where the Loess cap has been completely washed away leaving the underlying coastal plains material exposed. It was commonly observed on these bare spots that the planted pine trees would very early develop a yellow, stunted appearance and make very slow development for as long as seven or eight years. However, by this time most of the trees would have accumulated a small ring of leaf

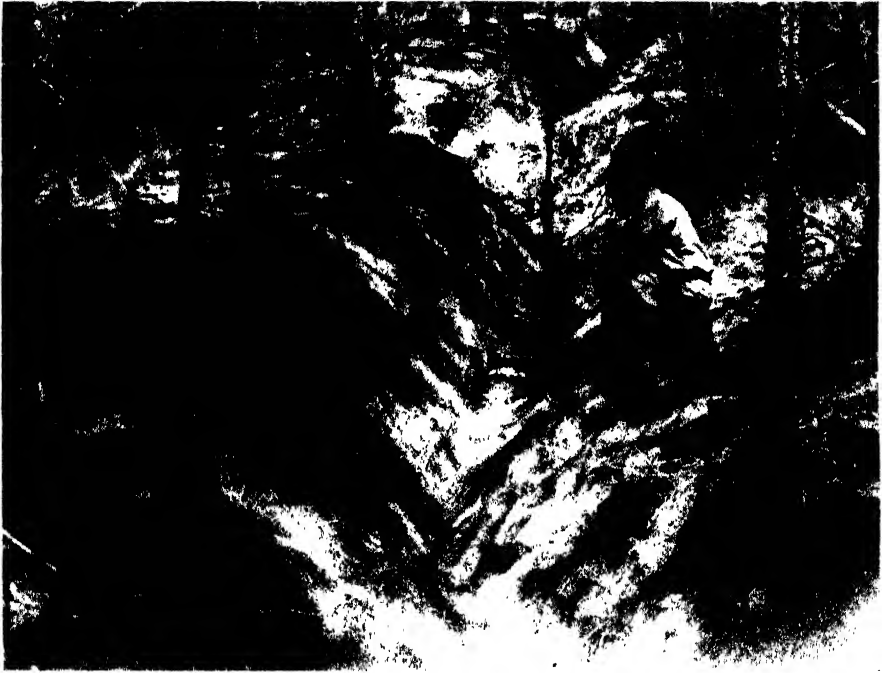


FIG. 5. Planting South Carolina 10 (Table 1) when the trees were eleven years old. Note the very fine ground cover on these unsloped gully banks.

litter, after which they consistently developed a more vigorous color and increased in rate of growth. Periodic observations on many of these galled spots indicates that eventually the trees will provide complete ground cover (Fig. 4).

There appeared to be no sharp correlation between degree of slopes and rate of development of ground cover. Unsloped steep gully banks were commonly found where a complete mantle of leaf litter covered the surface of the ground (Fig. 5). There was, however, a very definite correlation noted between the development of a complete ground cover and stabilization of the soil. Where this cover had been established, active erosion was no longer in evidence. This confirms the well estab-



FIG. 6. A gully control series. (A) Gully in April, 1935, just after black locust seedlings had been planted. (B) The same gully after five growing seasons. The area has been completely protected from grazing and fire.

lished principle that the major element in erosion control is a complete protective ground cover.

#### 5. DAMAGE BY INSECTS AND DISEASES

Considerable damage to young pine plantings by the pine-tip moth was observed on loblolly and shortleaf pine. Undoubtedly, the prevalence of this insect over the Southeastern Region materially retards the development of these species during the first six to eight years. Fortunately, mortality seldom occurs and the plantings eventually outgrow the effects of this insect.

The black locust borer (*Cyllene robiniae*) has done tremendous damage to black locust and appears to gain in population as the planting advances in age. This has occurred even in some of the more successful plantings. It is commonly observed that in plantings that appeared to be successful up to six to eight years of age, severe damage would become apparent rather suddenly. In many plantings with good initial survival and growth, the borer has so severely injured the trees that many main stems have broken off, giving the plantation the appearance of having been struck by a wind storm (Fig. 6).

The most commonly observed disease in these erosion control plantings, particularly on slash and loblolly pine (Fig. 7), has been the cronartium canker (*Cronartium fusiforme*). As much as 80 per cent of the trees in a slash planting have been found infected. Fortunately, severe infections of this character are very highly localized. In most parts of the region only a small per cent of the trees were found infected.

#### 6. EFFECT OF SITE PREPARATION ON SURVIVAL AND GROWTH

Unfortunately, it has been difficult to find plantings where an appraisal could be made of treated and untreated gullies with similar conditions. However, in the few cases where this was possible, the advantages of bank sloping, dynamiting, and check dam construction are not apparent. After a dozen years or more, treated and untreated gullies look about the same. Measurements of experimental erosion control plantings at the Soil and Water Conservation Experiment Station at Watkinsville, Georgia, failed to reveal significant differences in survival and growth of trees on treated plots and check plots over a period of seven years. The site preparation applied on the treated plots included furrowing, ridging, subsoiling, fertilization, cultivation, and mulching. The only exception was mulching, which did bring about a significant difference in survival and growth of trees on the treated and check plots.

#### 7. WILDLIFE OBSERVATIONS

Considerable use of these plantings by various forms of wildlife, particularly birds, was noted. Many different kinds of song birds and other species were seen in these plantings and numerous nests were found. In one pine planting in Kentucky a count of nests in the trees on a 1/10-acre plot indicated about 270 per acre. Cottontail rabbits were very frequently seen in both the pine and hardwood plantings.





FIG. 6, Part Two. (C) The same gully again as it looked after nine years. At this time there was considerable evidence of grazing and black locust borer damage. Note some broken trees. (D) The same gully in May, 1947, after twelve years. There are numerous signs of heavy grazing and severe black locust borer infestation. A planting that for some years appeared successful looks like a failure now.

### 8. RATE OF GROWTH

In general the rate of growth of the pine plantings has been very satisfactory over a wide range of site conditions. In sharp contrast to most of the black locust plantings the pine have consistently shown increasing vigor at each periodic study and an accelerated rate of growth, particularly in height. Black locust has failed in most plantings in the southeast. In Table 1 an attempt has been made to show typical plantings in various parts of the Southeastern Region. Included in this table are, with one exception, only those plantings that are on land use capability Classes VI and VII as classified by the Soil Conservation Service. This exception is Florida 1 which is on Class III or Class IV land. Classes VI and VII should be used only for permanent vegetation such as grass and trees.

The growth figures in Table 1 were secured by measuring the trees on 1/10-acre plots. In most cases all live trees on the plots were measured in inches and tenths to obtain average diameters. In determining average height, the general practice was to measure with a pole two rows of trees across the center of the plot at right angles. In computing the volume in cords, the mean sample tree method was used. Total cubic feet of wood on the plot, to a 2-inch top diameter, was first determined and then this cubic foot figure was converted to stacked cords by dividing by 90. On most of the plots measured no trees under 2 inches in diameter breast high were included in the volume computations.

The approximate numbers of posts produced were determined by estimating the number of posts in each tree on the plot. The post specifications used were: length, 6½ feet; minimum top diameter, 3 inches inside bark.

In reviewing the plantings listed in Table 1 it will be noted that there are some sharp variations in results. Some of these variations can be explained; others, on the basis of results thus far, are difficult to explain. Plantings Tennessee 1 and Tennessee 3 serve to illustrate that mixtures of pine and black locust do not work out satisfactorily. The chief reason for this is that on sites that are favorable for black locust the locust soon overtops and whips out the pine. On the other hand, where the site proves to be poor for black locust, which is generally the case in the Southeastern Region, the pine overtops the black locust. Planting Tennessee 3 on the table illustrates the exception.

Tennessee 1 is an example of a planting in a great system of gullies where the Loess cap has completely washed away leaving the bare Coastal Plain material exposed. Almost without exception, the growth on these sites has been very slow.

Plantings reported in the table and observations in general show conclusively that, of the species of pine represented, loblolly pine is the most satisfactory tree to plant in the Southeast for erosion control. In survival, in rapid early growth, and in the establishment of ground cover, it excels in all parts of the Region under consideration except in the extreme southern and northern parts. It is a compatible species to use

TABLE 1  
GROWTH ON TYPICAL PLANTINGS

PLANTING				GROWTH										VOLUME PER ACRE								
State	Species	Age	Soil-Slope	Ero- sion	Ave. DBH—Inches					Ave. Height—Feet					Cords			Posts				
					'41	'44	'45	'46	'47	'41	'44	'45	'46	'47	'44	'45	'46	'47	'44	'45	'46	'47
Tenn. 5	Lob. Pine	13	Ruston sandy loam—20 per cent	(9)	3.2	4.8	5.6	..	..	19	25	35	..	..	11	..	15	..	810	..	1,600	..
Tenn. 1	Mixed Lob. Pine B. Locust	13	Orangeburg- Ruston sand 25-30 per cent	(9)	..	..	3.9	..	..	6	10	..	16	..	..	..	..	..	..	..	..	..
Tenn. 3	Mixed Lob. Pine B. Locust	13	Grenada- Loring-silt loam—8 per cent	(9)	..	2.5	..	3.2	..	8	10	..	10	..	..	..	..	..	..	..	..	..
Ky. 8	Mixed Lob. Pine Shlf. Pine Va. Pine Pitch Pine	10	Memphis silty clay loam—8 per cent	48	..	..	..	..	..	7	14	..	18	..	..	..	..	..	..	..	230	..
Ky. 22	B. Locust	10	Loring silty clay loam— 7 per cent	4 (8)	..	..	2.4	..	..	11	15	17	..	..	..	..	..	..	..	..	210	..
N. C. 1	Lob. Pine	11	Wilkes fine sandy loam— 25 per cent	4 (8)	..	..	4.2	5.1	..	..	..	22	29	..	9.4	..	17	..	900	..	1,410	..
N. C. 9	Lob. Pine	11	Iredell clay loam—20 per cent	4 (8)	..	..	3.3	4.2	..	..	..	15	23	..	3.6	..	10.9	..	370	..	980	..

S. C. 2	Mixed Lob. Pine Slash Pine	13	Lloids clay loam—7 per cent		1.0	1.7 5.6 3.6	23	17 30 23	11	15	1,260
S. C. 10	Lob. Pine	13	Cecil—19 per cent	3 (7)		3.0		26		17	1,189
Miss. 2			Leau—sandy loam—18 per cent	3 (7)	1.3		23		8		900
Miss. 8	Mixed Lob. Pine Slash Pine	9	Loring silt loam—8 per cent	3 (7)	1.3 3.5 1.1		21		6.3		680
Ala. 6	Mixed Lob. Pine Slash Pine	11	Madison sandy clay loam—15 per cent	(7)		3.1 3.5 3.3		19 28 30		14	870
Ala. 12	Mixed Lob. Pine Slash Pine	10	Fullerton gravelly loam— 10 per cent	38		3.6 3.8 3.2		24 25 24		19	770
Ga. 1			Cecil sandy gravelly—5 per cent				13	12.5		6.6	
Fla. 1	Lob. Pine Slash Pine	9 12	Norfolk deep sand—3 per cent	3	1.0	1.5 5.1	26	28 38	12	14.3 23.7	1,380 1,930

Note: All plantings spaced 6 x 6 feet except South Carolina 10 which was spaced 4 x 4 feet. Age column denotes the age of the planting when last studied. The site was severely gullied in all plantings listed except South Carolina 2, Georgia 1, and Florida 1, which were moderately to severely sheet eroded. Erosion symbols are from Soil Conservation Service table of erosion classes.

in mixture with shortleaf in a large part of the central Southeast and with slash in the southern part of that Region. With numerous plantings of loblolly as far north as western Kentucky, central and western North Carolina, and central Virginia, there has been a good opportunity to observe its reaction to snow and ice and low temperatures. More damage in the form of winter browning and breakage of leaders and side branches



FIG. 7. Typical result of *Cronartium* canker infection on the main stem of planted slash pine.

has been noted on loblolly than on shortleaf and the northern species of pine. However, it has exhibited remarkable ability to recover from this damage. This, on the basis of observations thus far, indicates the possibility of expanding its use northward.

The use of slash pine in erosion control plantings was considered questionable at first. Results, however, have been rather encouraging as the figures indicate. While the survival has not been as good as either loblolly or shortleaf, the rate of growth has been very encouraging even in the northern part of the Gulf Coast States. One eighteen-year old planting in west Tennessee still shows vigorous growth, little or no apparent winter damage, and has some natural reproduction. Observations of ice storm damage in several plantings where slash was present along with loblolly and shortleaf disclose that it was damaged more than the others.

Shortleaf pine, while slower in growth than loblolly and slash, is a species that has survived and grown well all over the Region except in the extreme southern part. The use of shortleaf pine probably should be limited in those areas where this particular species is being attacked by a disease known as little-leaf disease.

The results of plantings with longleaf pine, which is one of the most adaptable and desirable species to plant in the southern part of the Region, particularly in the sandhill sections, have been very discouraging. This is due chiefly to low survival and delayed growth. Plantings are under observation where planted longleaf seedlings were found still in the grass after twelve years.

Both pitch and Virginia pine have proved to be very rugged species to plant on eroded sites in the northern part of the Region. It is felt, however, that due to their poor commercial quality they should be used as fillers in mixture with some one of the more desirable species such as shortleaf and white pine.

Unfortunately, very little white pine has been used in erosion control plantings. Observations of a few planted areas and of natural stands on eroded soils in western North Carolina, Virginia, eastern Kentucky, and Tennessee indicate, however, that it can be used more extensively than in the past.

Some Scotch pine used in Kentucky still shows vigorous growth after twelve years. A few cases of very successful red cedar one-row border plantings were observed. It is felt therefore that its use in this way should be more widely recommended.

Table 2 presents average growth figures by species of all plantings in which growth measurements were made.

#### SUMMARY

The observations and measurements of the early erosion control plantings in the Southeastern Region appear to justify the following summary statements:

1. Protection from both grazing and fire was found to be a major essential in the early establishment of a forest cover for conservation of

TABLE 2  
AVERAGE GROWTH PER YEAR, ALL PLANTINGS

Species	Diameter (inches)	Height (feet)	Volume	
			Cords per Acre	Posts per Acre
Black Locust . . . . .	.25 (15) *	2.2 (20)		18 (20)
Loblolly Pine . . . . .	.38 (38)	2.2 (44)	1.3 (24)	117 (18)
Slash Pine . . . . .	.40 (23)	2.5 (21)	1.2 (12)	114 (11)
Shortleaf Pine . . . . .	.24 (4)	1.3 (9)	.8 (2)	90 (1)
Longleaf Pine . . . . .	.27 (3)	1.6 (3)	.8 (1)	80 (1)
Pitch Pine . . . . .		1.1 (9)		
Virginia Pine . . . . .		1.3 (4)		

\*Figures in parentheses indicate number of plantings.

Note: Average age of plantings studied:

Black Locust—8 years; Loblolly Pine—11 years; Slash Pine—11 years; Shortleaf Pine—16 years; Longleaf Pine—15 years; Virginia Pine—8 years; Pitch Pine—7 years.

soil and water and for the production of wood. To encourage and preserve early natural invasion of both annuals and perennials, protection from grazing, particularly, and fire is required.

2. The pine species have survived and grown well universally, black locust and other hardwoods very poorly. Results indicate the advisability of close spacing—6 x 6 feet as an average, closer on severely eroded spots and gullies—to bring about the establishment of ground cover at an early date. A great deal of emphasis is needed on prompt survival examinations the first and second year after planting, followed by replanting as required.

3. Pine plantings over a wide range of conditions have established ground cover and completely controlled erosion in eight to ten years. Under some of the more severely eroded conditions, particularly on galled spots, many more years have been and will be required.

4. These observations tend to confirm that such insects as the black locust borer constitute a limiting factor in the use of black locust for erosion control plantings. Cronartium cankers were found very commonly but were confined mostly to slash and loblolly pines. In most cases observed infected main stems can be eliminated in the first thinnings without too seriously reducing density of stand.

5. In general, preparation of the planting site by plowing, furrowing, ridging, bank sloping, dam construction, etc., have not resulted in clear-cut advantages in terms of survival and growth.

## A RANGE TEST OF SPECIES ADAPTABILITY<sup>1</sup>

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One of the major considerations in artificially reseeding range lands is the selection of the species to be used. Not only must the species be adapted to the environment so that it can become established and maintain itself on the range; it must also be capable of producing substantial amounts of herbage necessary for grazing animals. Both plant numbers and herbage production show the degree of establishment and productivity of a species and serve to aid in determining its adaptability as a range forage plant. Other factors, such as palatability and resistance to grazing, influence the selection of a species as a forage plant and in a sense may reflect upon its adaptability for range use. However, as used here, adaptability refers to the ability of the species to become established, maintain itself, and produce substantial amounts of herbage.

A species adaptability test was begun in 1940 at the Ruby Substation of the Intermountain Forest and Range Experiment Station. The experimental headquarters area is ten miles west and south of Wells, Elko County, Nevada, and lies in the foothills of the Ruby Mountains. The drainage of these north-facing foothills is toward the Humboldt River and many of the small streams are intermittent, being fed from melting snow. The elevation at the headquarters is 6,000 feet. Average annual precipitation for the eight-year period ending in 1947 was believed to approximate 18 inches. Buried rain gauges read intermittently between May and October for the period averaged 134 per cent of the precipitation recorded for the same dates at Wells, which has an elevation of 5,633 feet. The average annual precipitation at Wells for the 1940-47 period was 13.45 inches which exceeded the 58-year normal of 9.68 inches by 3.77 inches. The growing season starts in April and ends in October, although freezing temperatures were recorded at Wells for every month in 1947. Most herbaceous species have dried by mid-July and pass through the normal summer drouth in a dormant condition. Fall growth and germination are dependent upon favorable temperature and moisture conditions.

The experimental area is within the upper limits of the *Artemisia tridentata* type. At this elevation in northeastern Nevada, typical species of the mountain brush zone such as *Purshia tridentata* and *Amelanchier florida* are found. *Populus tremuloides* descends from the higher range as stringers along the drainages. Much of the foothill range has been depleted of many of the valuable perennial forage grasses and forbs. *Artemisia*

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<sup>1</sup> Work described in this article was begun by Dr. J. H. Robertson, former range conservationist at the Intermountain Station, now at the University of Nevada, and continued by the author.



*tridentata* has increased on the overused ranges by invading the areas once occupied by the valuable perennial herbaceous species. *Bromus tectorum* characterizes the herbaceous understory where also are found occasional plants of *Poa secunda*, *Elymus condensatus*, *Agropyron spicatum*, and *Festuca idahoensis*. The most conspicuous perennial forb is the vernal *Balsamorhiza sagittata*. As a result of a range fire in 1940, practically all of the experimental area and much of the adjacent range was burned and *Artemisia tridentata* was eliminated. The fire-tolerant *Chrysothamnus viscidiflorus* which was mixed with the sagebrush became the most common shrub on the burned range. However, this species does not occur as frequently as did *Artemisia tridentata*.

The site of the test is in most respects representative of the general area and typifies much of the range land in northeastern Nevada. Prior to the fire the site supported a vigorous and dense stand of *A. tridentata*, lesser amounts of *Chrysothamnus viscidiflorus*, and the customary herbaceous understory. The soil is a deep, friable, dark loam built up largely from alluvial deposits by a small tributary to the central drainage system of the canyon. The soil is undoubtedly deeper and richer than that which might be termed typical of the adjacent range. As the topography increases in steepness, the soils become shallower and lighter colored, and rock outcrops are fairly frequent. The upper end of the planting site lies between a small ridge and the tributary drainage and slopes gently northward to a broader open area.

#### ESTABLISHMENT AND MEASUREMENT PROCEDURES

The selection of the thirty-eight species used in the adaptability test was based largely upon their performance in an adjacent nursery where 149 species had been planted. Species grown in the nursery customarily receive some cultivation to reduce competition from weeds and grasses—the purpose of the nursery being to test the responses of a large number of species to the soil and climatic conditions. However, the field plot test contained no provisions to reduce or control competitive vegetation; the species were thus subjected to more rigorous growing conditions. Further, both seedbed preparation and planting method simulated techniques used in large-scale range plantings.

Thirty-six species were drilled at 12-inch spacings in 1/100-acre plots in October, 1940. Since seed for two additional species was not available at that time, it was not planted until the following October. Assignment of species to plot was by random within each of two blocks. In general, seed size governed planting depth while rate of seeding was influenced by number of seeds per pound, growth characteristics of the species, and productiveness of the site. Since the ground surface was bare of vegetation as the result of the range fire in the summer, no additional seedbed preparation was used.

The average number of plants per square foot was determined for each species every year from 1941 through 1947. Current-year seedlings were not included in the counts since the observations were customarily

made before the onset of the normal summer drouth which would cause a high seedling mortality. Rhizomatous grasses by the nature of their vegetative spread soon formed sod or sod-like patches which precluded individual plant counts. Because such factors as merging or thinning of closely spaced plants would affect apparent numbers, minor fluctuation between years for a species was not considered to be of any particular significance. However, consistent increases or decreases reflected upon the adaptability of the species.

From 1942 through 1947, herbage yields were obtained for the most productive species. As herbage production declined because of thin stands or low vigor plants, yield measurements were discontinued.

#### PLANT COUNTS

Precipitation during 1941 was above the average for the 1940-47 period and was well distributed throughout the growing season. As a result many species had seedling stands which grew rapidly. Most of the grasses produced a light seed crop. With but one exception, all species were represented when an inspection was made in June, although number of seedlings varied considerably among species. Plant counts for all species are presented in Table 1.

Although all species had performed well in the nursery, it was apparent that some were not adapted to the more rigorous conditions of the field plot test. Competition from the aggressive *Bromus tectorum* began early and persisted through the years, although where plots supported full stands of the planted grass, as was true of *Agropyron cristatum* and *A. intermedium*, the annual brome was reduced in numbers or eliminated from the plot. *Chrysothamnus viscidiflorus* also was a competitor for soil moisture and made vigorous growth particularly on those plots having thin stands of planted species. *Artemisia tridentata* seedlings were present by 1944 in some of the plots, but their development appears to have been repressed by vigorous stands of grass.

Of the four pronounced sod-forming grasses—*Agropyron smithii*, *A. trichophorum*, *Bromus inermis*, and *Elymus triticoides*—*Bromus inermis* produced the most complete stand whereas the other three did not fully occupy the plots by the close of the 1947 growing season. The delay of a year in planting *Agropyron trichophorum* as well as the bunchgrass, *Hordeum bulbosum*, permitted competitive vegetation to become established. This altered the growing conditions for these two grasses and thereby tended to invalidate any direct comparisons with other species. Spread of all four sod grasses has been fairly rapid in the nursery where *Bromus tectorum* has been controlled at least partially by cultivation. When *Agropyron smithii* was grown under greenhouse conditions in competition with *Bromus tectorum*, Rummell (3) found the young wheatgrass plants failed to produce rhizomes.

The complete disappearance of *Bromus anomalus*, and *Elymus salina*, which in 1941 were well represented by seedling stands, clearly demonstrated their lack of adaptability. Likewise, those species

TABLE 1  
AVERAGE NUMBER OF PLANTS PER SQUARE FOOT FOR EACH SPECIES  
AND THE YEAR OF OBSERVATION

Species	Plant Numbers						
	1941	1942	1943	1944	1945	1946	1947
<i>Agropyron cristatum</i> .....	1.4	1.4	0.9	1.5	1.4	2.0	1.5
<i>A. inerme</i> .....	0.8	0.5	0.3	0.4	0.6	0.6	0.7
<i>A. intermedium</i> .....	1.6	1.7	1.0	1.5	1.4	2.0	2.0
<i>A. smithii</i> .....	0.9	0.4	0.3	sod	sod	sod	sod
<i>A. spicatum</i> .....	0.5	0.4	0.3	0.3	0.4	0.4	0.5
<i>A. subsecundum</i> * .....	1.3	1.4	0.5	0.6	0.5	0.4	0.3
<i>A. trachycaulum</i> .....	0.2	0.2	0.2	0.2	0.1	0.05	0.05
<i>A. trichophorum</i> .....	..	0.8	0.04	0.1	0.2	0.3	sod
<i>Arrhenatherum elatius</i> ...	0.4	0.6	0.3	0.3	0.6	0.6	0.6
<i>Bromus anomalus</i> .....	0.6	0.2	0.05	0.01	0.05	0	0
<i>B. carinatus</i> .....	1.2	0.9	0.3	0.2	0.2	0.01	0.01
<i>B. inermis</i> .....	0.8	0.7	0.4	sod	sod	sod	sod
<i>Balsamorhiza sagittata</i> ...	0.6	0.1	0.2	0.1	0.1	0.1	0.1
<i>Cercocarpus ledifolius</i> ...	0	0	0	0	0	0	0
<i>Dactylis glomeratus</i> .....	0.2	0.2	0.06	0.09	0.06	0.05	0.01
<i>Elymus canadensis</i> * .....	1.2	1.2	0.9	0.6	0.2	0.3	0.01
<i>E. glaucus</i> .....	1.6	1.2	0.8	0.9	0.7	1.1	1.0
<i>E. triticoides</i> .....	1.3	0.6	sod	sod	sod	sod	sod
<i>E. salina</i> .....	0.9	0.9	0.05	0.02	0.02	0	0
<i>E. virginicus</i> .....	0.5	0.4	0.2	0.09	0.06	0.1	0.02
<i>Festuca ovina</i> .....	0.6	0.4	0.2	0.05	0.1	0.2	0.3
<i>Hesperochloa kingi</i> .....	0.5	0.02	0.1	0.07	0.1	0.2	0.2
<i>Hordeum bulbosum</i> .....	..	0.3	0.05	0.2	0.2	0.2	0.05
<i>Koeleria cristata</i> .....	0.1	0.03	0.02	0.06	0.08	0.1	0.1
<i>Lupinus ornatus</i> .....	0.5	0.4	0.4	0.3	0.3	0.3	0.2
<i>Michels rye</i> .....	0.9	1.1	0.1	0.1	0.04	0.08	0.1
<i>Medicago sativa</i> .....	0.3	0.2	0.1	0.2	0.2	0.1	0.01
<i>Oryzopsis miliacea</i> .....	0.4	0	0	0	0	0	0
<i>Penstemon palmeri</i> .....	0.9	0.8	0.05	0	0	0	0
<i>Phalaris arundinacea</i> .....	0.01	0.03	0.05	0.05	0.01	0.01	0.01
<i>Phleum pratense</i> .....	1.1	1.0	0.4	0.4	0.5	0.5	0.2
<i>Poa ampla</i> .....	0.3	0.2	0.2	0.2	1.1	0.8	0.8
<i>P. nevadensis</i> .....	0.1	0.05	0.05	0.1	0.1	0.2	0.3
<i>P. secunda</i> .....	0.1	0.01	0.01	0.07	0.06	0.1	0.1
<i>Purshia tridentata</i> .....	0.7	0.03	0	0	0	0	0
<i>Stipa comata</i> .....	0.1	0.01	0	0	0	0	0
<i>S. columbiana</i> .....	0.4	0.2	0.2	0.1	0.3	0.3	0.3
<i>S. lettermani</i> .....	0.2	0.1	0.05	0.2	0.1	0.2	0.2

\* Counts based on one plot only.

having thin stands as a result of consistently decreasing plant numbers indicate their intolerance to the growing conditions. Competition and the accompanying decrease of available soil moisture were not the sole factors influencing the failure of a species. The disappearance of both *Oryzopsis miliacea* and *Penstemon palmeri* was attributed directly to winterkilling. Lack of an initial stand for *Cercocarpus ledifolius* suggested that such factors as low seed viability or refractory germination were responsible for the absence of seedlings. Hence the adaptability of this species was not determined by the test.

Since *Purshia tridentata* and *Balsamorhiza sagittata* appeared in the native vegetation, they were unquestionably adapted to the soil and climatic conditions. Weather factors prevailing during the trial or the intense competition of *Bromus tectorum* plus the relatively slow rate of growth for both species were believed to be influential in the disappearance of *Purshia tridentata* and the decrease in plant numbers of *Balsamorhiza sagittata*. Nursery plantings of *Purshia tridentata* have yielded fair to good stands when some degree of cultivation was practiced. However, observations made in northern Nevada have failed to reveal established seedlings near parent plants in dense stands of *Bromus tectorum*.

The successful establishment of volunteer plants by some species increased plant numbers in the later part of the test period. Notable in this respect was the substantial increase of *Poa ampla*, and to a lesser extent that of *Agropyron inerme* and *Arrhenatherum elatius*. Such a characteristic demonstrates the aggressiveness of these species when subjected to the full influence of competitive vegetation. In contrast, a number of species including *Koeleria cristata*, *Poa nevadensis*, *P. secunda*, and *Stipa columbiana* which had thin initial stands failed to show any material increase in plant numbers. Lack of aggressiveness by a species may limit its usefulness as a range forage plant.

As judged by plant numbers, the adaptability of a species is best exemplified by a satisfactory seedling stand and the persistence of these plants through the year, combined with good seeding or propagating habits. Both *Agropyron cristatum* and *A. intermedium* demonstrate these qualities. Volunteer seedlings were present on the plots of these grasses but the density of the stand and apparent total occupation of the plot by older plants prevented the establishment of seedlings. The mildly rhizomatous habit of *A. intermedium* was further influential in closing the stand to seedling establishment.

#### HERBAGE PRODUCTION

Plant numbers in themselves usually cannot be relied upon to indicate the merit or adaptability of a species as a desirable range forage plant. The vigor of the plants as reflected in their diameter, height growth, and herbage production is of importance. To arrive at a more complete measure of adaptability, herbage yields were used. The average yields from two plots for each species for the six-year period are found in Table 2.

The two highest yielding species over the six-year period have been *Agropyron cristatum* and *A. intermedium*. The former has been widely used in range and dryland pasture plantings throughout much of the West. Its high productivity and wide range of adaptability plus drought and grazing resistance combine to make it a valuable range plant. Eighteen-year-old stands in Montana have yielded from 1,600 to 2,000 pounds of field-cured hay per acre (5, 6). Although the adaptability of *A. cristatum* was fairly well known, its inclusion in the test was used to some extent as a standard with which to compare other species. *A. intermedium* has

TABLE 2  
AIR-DRY YIELDS IN POUNDS PER ACRE FOR SPECIES PLANTED OCTOBER, 1940

Species	Year						Ave.
	1942	1943	1944	1945	1946	1947	
<i>Agropyron cristatum</i> .....	1,512	603	690	983	1,267	1,542	1,098
<i>A. inerme</i> .....	188	136	274	...	1,000	990	518
<i>A. intermedium</i> .....	515	479	713	940	1,383	1,606	911
<i>A. smithii</i> .....	...	72	150	...	...	...	111
<i>A. spicatum</i> .....	...	167	...	...	...	...	167
<i>A. subsecundum</i> * .....	863	351	229	...	...	...	481
<i>A. trachycaulum</i> * .....	...	319	...	...	...	...	319
<i>Arrhenatherum elatius</i> .....	1,249	252	122	...	900	740	713
<i>Bromus carinatus</i> .....	916	67	...	...	...	...	492
<i>B. inermis</i> .....	714	444	378	360	900	192	548
<i>Elymus canadensis</i> .....	609	279*	108*	...	...	...	332
<i>E. glaucus</i> .....	598	358	229	297	217	334	339
<i>E. triticoides</i> .....	68	117	...	...	...	...	108
Michels rye .....	137	4	...	...	...	...	220
<i>Poa ampla</i> .....	345	165	398	655*	867	1,058	581
<i>Phleum pratense</i> .....	682	200	...	...	...	...	441

\* Yields from one plot only.

not been used in Nevada or adjacent states until fairly recently and then has been confined to small experimental tests. As yet sufficient quantities of seed are not available at a reasonable enough cost to permit large-scale plantings of this promising wheatgrass. *A. intermedium* has been slower to reach full development than *A. cristatum*, and although the latter produced more herbage, statistically there was no significant difference in yields. Somewhat similar development rates were found between these two species by Robertson (2). Both of these introduced grasses proved superior to the highest yielding native grasses—*Agropyron inerme*, *Elymus glaucus*, and *Poa ampla*.

Both *Arrhenatherum elatius* and *Bromus inermis* have been used in eastern and midwestern pastures as well as in irrigated pastures in the West. Under favorable soil and moisture conditions these two grasses have proved to be well suited to range plantings, especially at the higher elevations. The ability of *Arrhenatherum elatius* to develop rapidly, as seen by the high yield in the second year, together with early spring growth makes it a desirable forage plant wherever it is adapted. Tests in eastern Oregon showed that this species was outstanding in herbage production during a three-year period (1). However, such a consistently high yield was not experienced in this test. An increase in later years resulted from a thickening of the stand by volunteer plants.

*Bromus inermis* has formed a dense sod that has largely excluded the annual *B. tectorum*. Yields have never been as great as those for some of the other species although the grass will grow and maintain itself. However, when either or both *B. inermis* and *Arrhenatherum elatius* were planted in mixtures with *Agropyron cristatum*, in other studies at this station, both species soon became infrequent constituents of the stand.

*Agropyron inerme* and *Poa ampla* were comparable in that both reached highest productivity toward the end of the test period. For both grasses an increase in plant numbers appeared to be influential in the increase in yields, particularly with respect to *P. ampla*. Establishment of satisfactory seedling stands has been a problem with this grass (1), although in southern Idaho fall planting on summer-fallowed ground has resulted in good initial stands (4). Development of *Agropyron inerme* has been slower than that of *A. cristatum* as found here and in other studies in northern Nevada. Stark, *et al.* (4) found that five-year-old stands of *A. spicatum*, closely related to *A. inerme*, yielded approximately the same as *A. cristatum* but yields from younger stands were lower. In addition to this seemingly inherent, slower development rate, the competition from *Bromus tectorum* was believed to be influential in repressing the growth of *Agropyron inerme*. Present stands are largely free of *Bromus tectorum*, especially in the area of domination around each of the large wheatgrass plants. Hence a slower growing species which is further retarded by competition may be limited to some extent in its use for range reseeding.

*Elymus glaucus*, although well represented by plant numbers in the seedling stage as well as in later years, has not produced high yields. From observation the general vigor of this grass has been low and this has been reflected in the yields. Competition from other species in the plot, notably *Bromus tectorum*, have held it in check and warrant its rejection as an adapted species.

As was clearly shown in Table 2, many of the species which in the earliest years of the test were fairly productive and appeared promising did not persist. Those species which had relatively high initial yields might prove desirable in the establishment of temporary pastures under such conditions but could not be expected to remain as constituents of the permanent vegetative cover in range plantings.

#### SUMMARY

Of thirty-eight species tested for adaptability near Wells, Nevada, one failed to emerge, six failed to persist, while thirteen decreased in plant numbers to an extent that rendered them undesirable for permanent range cover. Seven additional species had thin stands in which plant numbers failed to increase materially, indicating their lack of aggressiveness. Stands of *Arrhenatherum elatius*, *Agropyron inerme*, and *Poa ampla* were thickened by the establishment of volunteer plants. *Agropyron cristatum* and *A. intermedium* had good initial seedling stands and maintained high plant numbers throughout the period. Of the four pronounced sod-forming species, only *Bromus inermis* had fully occupied the plots by 1947.

Over a six-year period, *Agropyron cristatum* produced an average yield of 1,100 pounds of air-dry herbage per acre followed by *A. intermedium* with 940 pounds, although these differences were not significant. The rate of development of *A. intermedium* was slower than for *A.*

*cristatum*. *Arrhenatherum elatius* ranked third in herbage production with greatest yields occurring in the second season. The next four highest producing species were *Poa ampla*, *Bromus inermis*, *Agropyron inerme*, and *Elymus glaucus*. In general, yields of *Poa ampla* and *Agropyron inerme* have increased during the test period. *Bromus inermis* was not a consistent producer of substantial amounts of herbage. Relatively low yields throughout the test have been a characteristic of *Elymus glaucus*.

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# JUDGING RANGE CONDITION AND TREND IN A RANGE INVENTORY PROJECT

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Today the range manager charged with the responsibility for maintaining and improving extensive grazing lands and critical watersheds is using new and promising methods in the accurate determination of the condition and trend of the range. There has been more and more analysis of the many things comprising the whole range environment including physical and biological elements. These "fine points" of range stability and balance have been skillfully presented for wider understanding and acceptance. Much remedial action taken in past years to increase forage volumes and to halt erosion has not achieved the results expected, because of our failure to recognize the incipient actions operating where the natural environment has been disturbed.

In the new and objective sense, range condition is the relative position of a given range in comparison with an accepted standard of maximum development. It is aptly termed "range health" and a rather definite description of the ideal or topmost management objective must be used in order to give significance to any one definition of condition.

Range trend is a term suggesting movement or change, specifically the change toward a standard objective condition or away from it. A trend is toward better condition—upward, or toward poorer condition—downward. The basis for determining the direction is an understanding of all the elements making up the ecology of the range.

Logically, it is a function of range inventory projects to determine range condition and the trend in condition. The summation of forage densities and volumes is not enough if there is not an expression of the quality of the range in comparison with some known ideal, and if the trend in condition is not recognized and incorporated in management plans.

The following is a discussion of a method for including condition and trend studies in the range inventory procedure, and for evaluating the range resource with exact evidence in matters of range stability and trend.

Actually range inventory may be expected to reveal and describe the gap between existing condition and some anticipated standard of good range condition even before that *good* range condition is well defined. It is that position much of our range inventory work is in because it has not yet been possible to describe the many condition classes and trend indicators we would like to have for all forage types (Figure 1). However, we must begin to apply our known aids as fast as possible, especially



to the one problem of adjusting the stocking rates we will apply to range inventory forage data.

In the past the determination of a stocking rate has often been based erroneously, though in good faith, on records of past use and an inaccurate mental picture of good range. Subsequent detailed study has revealed that the selfsame range might fall into a poor classification on ecological bases, and actually may be in a downward trend due to a progressive soil loss and soil instability.



FIG. 1. It should be a function of range inventory work to record the definite differences in condition in these two meadows.

Range surveys have long been confronted with the problem of obtaining stocking rate figures which are taken from ranges in definitely good condition or computed for a definite upward trend in condition. Some investigators say that a safe stocking rate expressed as surface acres per animal month should be determined for each condition class within major forage types. Research agencies have developed such classifications and have recommended stocking rates for some range types and vegetation climax groups. These are proving to be the practical approach to the stocking problem.

But to what extent can range surveys incorporate the new concepts and truths in those types where no definite condition classes have been determined? It is unsafe to go beyond a very general rating for these types, and evidence is not available for assigning numbers of animal months or seasons of use until we know what the resistance and recovery potentials are for each forage climax. Our concepts of utilization standards and the proper use values we assign to individual species are likewise tied up with the variations in condition and direction of trend. To what extent may we rely on present values?

Where range inventory work is concerned, either the condition classes and stocking rates must be well developed for the direct compila-

tion of carrying capacities, or else the data obtained with use of the new concepts and indicators must be relegated to the more general function of aiding in the adjustment of stocking rates obtained from other sources.

The methods employed in gathering condition and trend data in connection with range surveys in the Blue Mountains of Oregon and southeastern Washington are described below.

### THE FIELD PROCEDURE

The range inventory conducted by the Forest Service on the mountain ranges of the Umatilla National Forest in 1947 employed the Reconnaissance Method of Range survey and used the standard techniques recommended for estimating forage densities and vegetative composition.

The examiners used aerial photographs in the field and drew forage types directly on the photographs. They used hand stereoscopes to study the terrain and to make general interpretation. In addition to the photos and the writeup sheets normally used, the men carried a supply of condition and trend analysis forms for use on open dry grassland types (Type 1), and mountain meadows (Type 2). Whenever the men mapped these types in making their regular forage estimates, they remained long enough to make a writeup for the indicators of soil and forage condition on a check list developed for the purpose by the Regional Forester. See Figure 2.

The idea of using a check list for a record of these observations has been developed by investigators in several ways and in each case there has been an attempt to facilitate a comprehensive study of as many of the elements of soil and forage condition as possible. The interactions and variations between the indicators are so varied and their influence on each other so interlaced that some simple method of recording the individual items for deliberate study is needed.

It will be seen on a moment's examination that this check list does not provide for qualifying a type into a particular condition class; it does however, develop definite answers on stability or instability in the range complex and provides for analysis of the *trend* in condition. This treatment was necessary because of the lack of fully accurate concepts of the ecological succession in the bunchgrass or timber range typical of this area. Excellent standards were at hand for the determination of condition classes on mountain-meadows using plant indicators and these were quite adaptable to the record form (2). Most of the bunchgrass types encountered in this survey were either on open, rather flat-topped ridges or on extremely steep south slopes. Elevation varied from 2,500 feet in the canyon bottoms to 5,500 feet on the flat-topped ridges. Topography can be characterized as rough because of numerous small canyons running back from the main drainages, and because of steepness of side slopes.

In order to provide at least some basic information on the characteristics of these dry grasslands, a very general description of the good class and the poor class was prepared from existing information on plant suc-

## RANGE INVENTORY-CONDITION &amp; TREND, ANALYSIS FORM

Project No. Examiner Date

Type Location  
(Aerial Photo No. — Township & Range)

## Soil Condition Indicators

*Stability*

1. Normal density of cover.....
2. Normal litter of type.....
- °3. Invasion of openings by.....  
perennials. (List)
- °4. Invasion of erosion pavement.....  
by perennials. (List)
5. Soil remnants sloping sided.....
6. Healed gullies .....
- °7. Stabilized alluvial deposits.....
8. ....

*Instability*

9. Abnormally bare soil.....
10. Trampling displacement.....  
(current)
11. Abundant annuals .....
12. Rill marks .....
13. Active gullies .....
14. Active gullies originating in.....  
type.
15. Recent alluvial deposits.....
16. Erosion pavement .....
17. Soil remnants steep sided.....
18. Recent rodent work .....
19. Sheet erosion .....
20. Recent aeolian deposits .....

## Forage Condition Indicators

*Positive Value*

21. Desirable species abundant.....
22. Desirable species accessible.....
23. Desirable species vigorous.....
- °24. Desirable species invading.....  
openings. (List)
25. Desirable species reproducing
26. Several years' regrowth on.....  
hedged browse.
27. ....
28. ....

*Negative Value*

29. Undesirable species abundant.....
- °30. Undesirable species invading.....  
openings. (List)
31. Undesirable species repro- ..  
ducing.
32. Browse hedged .....
33. Browse high-lined .....
34. Excessive utilization ..  
of undesirable forage species
35. Plant relics present ..  
(List plants)
36. ....

Emphasis for indicators: A (not exceptional), B (pronounced very strong), C (very weak), blank (no observation). (°) Positive invasion determined by presence of age classes.

Does the type appear to have sufficient cover for soil stability?.....

Is the type producing its maximum of forage?.....

Percentage of bare ground surface covered by litter.....

What do the facts indicate as to trend in condition: 1. Soil.....

2. Forage.....

FIG. 2. Sample form developed for the survey.

cession in the region, and from observations on study plots correlated with the judgment of range managers. The two condition extremes were described as follows:

**Good Condition      Plant Density      .5 and up**

Bluebunch wheatgrass, *Agropyron spicatum*, is the most plentiful grass, Idaho fescue, *Festuca idahoensis*, is conspicuous. Sandberg bluegrass, *Poa secunda*, is present as an understory and does not make up a conspicuous part of the stand. Weeds form a very small percentage of the cover. Good distribution of age classes of the wheatgrass and fescue is present.

Soil is stabilized. It is friable, contains humus. Litter from several seasons growth is present. Young plants of the key forage species are invading bare areas. Sandberg bluegrass is not on soil pedestals. Important grasses are vigorous. Accelerated erosion is practically absent.

**Poor Condition      Plant Density      .1**

Bluebunch wheatgrass and Idaho fescue are greatly reduced in quantity and vigor and sometimes totally absent. Sandberg bluegrass is invariably the chief grass. Weeds such as yarrow, *Achillea lanulosa*, tarweed, *Madia glomerata*, eriogonum, *Eriogonum* spp., pussytoes, *Antennaria* spp., and wyethia, *Wyethia* spp., are very common.

Litter is slight. Sandberg bluegrass occurs on pedestals 2-3 inches high above a fully developed erosion pavement. Rills, small gullies and alluvial deposits are present. Few perennial grasses are found invading erosion pavement. Perennial weeds may be present.

### TRAINING THE CREW

Armed with record forms, photographs, memoranda on basic type classification, and reminder lists for indicators of conditions and trend, the crew is equipped for field work. Up to this point however, no mention has been made of training the men. Actually the training given a range inventory crew at the beginning of the field season is one of the most important phases of the project. Along with packing a great deal of new basic information into a few days of instruction, it is necessary at the same time to develop enough proficiency in the techniques of estimating and observing to get reasonable uniformity of judgment in a crew of men. One important skill to be developed is judging the density in percentage of ground covered and of judging the percentage of each species in the total vegetation. With the adoption of the condition and trend studies, the powers of observation had to be carried beyond any previous degree of proficiency.

It was not necessary to bring in new techniques of instruction or to use elaborate devices. A closely organized schedule was prepared to cover the subjects and to include as much practice as possible. The approved techniques adapted to many kinds of job instruction, including the elements of (1) discussion, (2) demonstration, (3) application, and (4) examination, were applied successfully. Training was in the field close to examples of many of the indicators studied, and the training tied in naturally with the range survey procedures.

There were six men in the crew. Of these, two were graduates in range management with past experience in range survey work, two were students of range management with some background work in range

ecology and field experience in forestry, and two were wildlife technology majors with little or no training in ecology. Though their experience background was varied and not too strong in the important matters of livestock husbandry, habits of grazing animals and ecology, they were all receptive to the theories of a delicately balanced range complex, believed in them, and tried to carry observations through to unbiased conclusions. Most of the indicators of range stability are objective and material things which the examiner can see and which are defined and pointed out in everyday terms; therefore, men with an interest in the work can learn the mechanics of the system rather easily.

Probably the most important device or technique of instruction is that of drawing comparisons between what is seen and what is believed to be an optimum topmost position in the condition ladder. Attainment of a concept of good range is a goal to strive for, and the best way to reach it would, of course, be a chance to see undisturbed range in its pristine state.

In the absence of good examples of the management objective, the instructors must call up skill enough to paint the word-picture of range at its best with soil stabilized, erosion scarcely visible, presenting good profile development, and supporting a maximum growth of the choice forage species of the region. Very often some stage in secondary succession or upward trend can be pointed out by looking at study plots closed to grazing, or by going to the inaccessible or unusable areas which have been subjected to very little or no grazing. The crew on this project worked with the latter kinds of study areas in the case of the open dry grassland types, and had a good opportunity to study all the main condition classes and indicator plants in the mountain meadows. It seems logical to assume that an opportunity to see good range in one kind of major type, such as meadow, does help the trainees to understand the probable appearance of good condition in another kind of type. This does not mean the adoption of the selfsame indicators for application to all types, but rather a development of the man's reasoning powers and his faith in the existence of an "ideal."

In order to attain the desired uniformity in thought throughout the crew, it was necessary to take up each individual indicator element as a separate study and point-by-point identify and emphasize its true meaning. This became a hands-and-knees phase of the instruction in which minute examination was made of sample areas and carefully selected examples. It was here that the greatest use of comparison was made and where differences of opinion were resolved. The size of the area examined varied with the locality, but on bunchgrass range the sample units were usually about one-half acre in size, selected to get a representative portion of the type. The men moved freely over this sample area and after careful study recorded the degree of emphasis each element should have in the whole picture of stability or instability. As differences of opinion showed up between the men there was opportunity to point out clearcut examples of the particular indicator, tie it into a concept of the ideal, and in general increase the powers of observation in the men.

Following the writeup of a sample area the group discussed the facts to agree on the trend in condition as indicated, the significant points were weighed against one another, and a resulting decision was made.

A summary of brief definitions based on the use of indicators in the Intermountain Region was used to preserve the identity and individual meaning of each of the elements used in the form. (1)

1. *Normal density of cover*—as judged by a comparison with an area in good condition.
2. *Normal litter for type*—as compared with an area in good condition.
3. *Invasion of openings by perennials*—new plants in bared soil where no erosion pavement has been formed.
4. *Invasion of erosion pavement by perennials*—new plants on a bare area having definite erosion pavement.
5. *Soil remnants sloping sided*—soil pedestals rounded and healing. Roots not freshly exposed.
6. *Healed gullies*—vegetation established on sidewalls and in bottom. No recent cutting.
7. *Stabilized alluvial deposits*—vegetative cover complete, perennial plants, litter.
9. *Abnormally bare soil*—as compared with an area in good condition.
10. *Trampling displacement, current*—this year, soil moved by hoofs of livestock or game.
11. *Abundant annuals*—weeds or grasses when they form a major portion of total vegetation.
12. *Rill marks*—very small gullies.
13. *Active gullies*—bare sides, recent cutting action in bottom.
14. *Active gullies originating in type*—limited to those gullies actually starting in type.
15. *Recent alluvial deposits*—soil picked up and moved short distances and laid down again right on the range.
16. *Erosion pavement*—the small rock or gravel left at the surface of the ground as result of the erosion and removal of soil particle.
17. *Soil remnants steep-sided*—vertical soil pedestals, exposed roots.
18. *Recent rodent work*—soil disturbance, relative abundance, compared with range in good condition.
19. *Sheet erosion*—loss of top soil over extensive areas, rills, erosion pavement starting.
20. *Aeolian deposits*—soil moved by wind to depressions or around plants.
21. *Desirable species abundant*—in comparison with an area in good condition.
22. *Desirable species accessible*—within reach of livestock.
23. *Desirable species vigorous*—as compared with normal growth form of the spp.

24. *Desirable species invading openings*—presence of new plants one or two years old in openings.
25. *Desirable species reproducing*—age classes present.
26. *Several years regrowth on hedged browse*—growth after grazing has been reduced.
29. *Undesirable species abundant*—weeds, annuals, species of low forage value—compared with range in good condition.
30. *Undesirable species invading openings*—presence of new plants one to two years old in bare openings.
31. *Undesirable species reproducing*—age classes present.
32. *Browse hedged*—repeated removal of all current years growth to develop a twiggy, rounded appearance.
33. *Browse high-lined*—absence of twigs and leaves on lower part of tall shrubs or trees to the height reached by livestock or big game.
34. *Excessive utilization of undesirable forage species*—utilization of current years growth on undesirable species beyond what is normally taken under good range condition.
35. *Plant relics present*—remnants of former vegetation.

#### THE SUCCESS OF THE WORK

The method was intended to be simple and adaptable to the reconnaissance survey job as a whole. In effect, it was a reconnaissance of the state of health of the most important types. It was not a soils survey nor an exhaustive ecological study, but it did identify the key points significant in the preparation of a management plan.

Check sheets were prepared for a total of 139 bunchgrass types and for 59 meadow types. These types corresponded exactly with those mapped on photographs for the grazing maps. Eighty-seven of the 139 bunchgrass types or about 63 per cent were definitely in poor condition, even by the extreme standards set up for the project. The remainder were judged to be fair, with densities between .2 and .4 and grass making up 50 per cent or more of the composition. On the other hand, 60 per cent of the meadows were found in fair condition and many were in an upward trend.

A number of interesting things were revealed during the course of the work, and among them were the purely "human" elements as well as actual difficulties in making the sheet work. Also, an encouraging uniformity of results has justified the use of the sheets in subsequent compilation work. There are a few things to think about and to iron out.

A downward trend in the soil condition accompanied by an upward trend in forage quality and volume was an observation made quite frequently. The men had been fully instructed in the reasons why this might happen and they made the decisions with confidence and the exercise of good judgment. They recognized a lack of stability in the range complex.

However, there seemed to be a persistent overuse of the term "static" to denote range on which the trend of condition was neither up nor down. This may have been caused by several things. The instructors, of course,

admitted the possibility that indicators might counteract each other so as to make trend very difficult to see, but there was no attempt to make "static" a category in itself. The men may have actually believed a static condition was indicated, but it was more likely that they turned to the general use of "static" in cases of doubt. They found it difficult to decide on trend when a great deal of variation in the type was encountered. They may have overlooked the shift in outside influences such as varying grazing intensity, or other factors. They saw specific examples of conflicting things—soil disturbance, soil stability, poor plants invading, and desirable plants invading—to the extent that they sought an "average" interpretation and missed the few really significant signs.

The adoption of a definite sampling technique using a predetermined size and frequency of study plots may be an answer and partial solution to the above difficulty.

It is also probable that during the training period the men were not sufficiently impressed with the living and changing quality of the range complex. Follow-up instruction was carried on throughout the inventory season to some extent, and in some cases it was possible to point out reasons why the trend should be changed from "static" to downward or upward.

The checksheet became easy to use as the men gained familiarity with the indicators and with their positions on the page. They were soon able to check off some of the elements which proved repetitious or weak in indicator value. For example, item 26 in the sheet was usually checked very weak wherever browse occurred. Item 20 was usually scratched because aeolian deposits were not common in the types surveyed. The men began to depend on certain of the items for greatest indicator value and those having to do with "invasion of openings" were important.

In a system of this sort there may be an urge to make the decisions on a purely numerical basis. Where indicators are quite obvious, as on very poor eroding sites, the marking shows up clearly for instability and negative forage value. The recorder is impressed by the preponderance of strong symbols on the bottom half of the sheet. If, on the other hand, he has a type in which the strong symbols are more inconsistent and scattered, he may be influenced simply by the longest list of strong points—whether it be for items of stability or for instability. An adding-machine technique cannot be applied in this system because the indicators may have varying significance. A careful analysis is always necessary.

The changes in floristic composition and surface soil as the weeks passed and the survey progressed had some influence on the observations. Some of the annuals all but disappeared and it required real search to find and to reconstruct them. The tiny rills and alluvial deposits created by spring runoff lost their identity, due to drying and crumbling of soil and trampling of livestock. Bunchgrass cured and lost some of its appearance of vigor, and the utilization of forage by livestock was important. A number of examples of change in the aspect of a type could be cited. These factors should be given some consideration in training and in later



check training. The progressive change due to advancing season affects forage volume estimates as well, and is provided for in the survey procedure.

It has been encouraging to note that results of the work were consistent. The men all used the plant indicators in very much the same way and saw the same plants. There was little confusion over how the work should be done. The sheets have served to put definite and comparable information in a simple form, and they have an excellent description value for permanent records. The data should be valuable for the application of protective and conservative stocking rates and should be used to demonstrate the improvements obtained from good management. In this survey they showed that many range areas are definitely in downward trend, and they also upheld the improvement which has started in some mountain meadows with reduction in sheep use.

If follow-up inspections and studies are made on a few of the major type areas by the chief of party or by range managers who are widely familiar with the types in the area, the extensive records made rather hurriedly by crew members will be substantiated and their reliability will be known. Providing these checks are made, the condition and trend of the range can be determined in range inventory projects with reasonable accuracy.

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# EARLY RESEARCHES IN THE RELATIONS OF FOREST FIRES AND UNUSUAL WEATHER CONDITIONS, HUMIDITY, DUFF MOISTURE, AND INFLAMMABILITY<sup>1</sup>

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Researches directed toward a discovery of the relations which exist between weather conditions and the intensity and rate of spread of forest fires date back to the years 1913 and 1914. Forest fires have destroyed millions of acres of timber, especially in the far western states. During the first two decades of the present century uncontrollable conflagrations had blackened large areas in California, Oregon, Washington, and Idaho, beginning with the Columbia National forest fires in 1902, sweeping over huge areas in Idaho in 1910 and again in 1919. Strangely enough, the intervening years from 1911 to 1918 inclusive were marked by few fires and rather favorable or safe weather conditions.

In view of the critical situation and the great disparity in the forest areas burned, forest officials eagerly sought to obtain information which would reveal what elements of or fluctuations in the climatic factors brought on these disastrous results. It is not strange therefore that the United States Forest Service appealed to the United States Weather Bureau for assistance in solving these problems, and that in 1916 the Forest Service sent to the various western forest experiment stations urgent appeals to begin forest fire weather research. During the years of their beginning, from 1910 to 1916, these stations had been equipped with fairly complete sets of weather instruments loaned by the Weather Bureau.

## FIRST ATTEMPTS AT SOLVING THE FOREST FIRE-WEATHER PROBLEM

An early report by Jesunofsky (2), is of interest in dealing with the state of weather preceding the very critical 1910 forest fire season. Jesunofsky states: "The principal agency . . . was the great deficiency in rainfall over nearly the entire western country beginning early in spring and continuing throughout the summer months. The averages of the accumulated minus departures in precipitation over the upper Mississippi Valley during the consecutive periods from March to August 29 were: —2.4 inches to April 25; —3.8 to May 30; —6.6 to June 27;

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<sup>1</sup> Foresters throughout the United States are now fully aware of the intimate and direct relations which exist between critical forest fires and low atmospheric humidity, for its realization has very significantly contributed toward a better directed fire prevention and control program. The author is very happy to give credit to the men who did the early spade work on the project and to have had a share in this important line of forest research.

—7.5 to July 25; and —9.5 to August 29. Deficiency for the upper Missouri Valley showed —7.4 inches, and the Rocky Mountain region —3.1. (In this article nothing was said about wind, temperature, relative humidity or pressure as contributing causes.)

The United States Weather Bureau responded with reports from E. A. Beals (1) and H. E. Williams (9). Beals, being then in charge of the California section of the Weather Bureau, stated that forest fires could be averted or better controlled if the winds could be foretold, especially by a study of the types of winds, their direction, and inward and upward movements; that the forecaster should be able to predict the general movement of the air over a large area, and that the forest ranger on the ground could apply this information locally. Beals said that the Hinckley fire of 1894 in Minnesota was preceded by two months of drouth, culminating in high temperature and pressure with strong winds blowing toward a low area; that during the Columbia National Forest fire in 1902 the winds blew westward from a high pressure area over the Columbia Plateau, and that the thermometer reached 90° on the western slopes of the Cascade Range, with a progressive decrease in the relative humidity. Preceding the disastrous fires in Idaho in August, 1910, there were long periods of drouth and high temperatures, but not much wind movement. Beals did not discuss wind movements generated by the fires themselves. He recognized that low humidity accompanied fire-weather but did not impute special importance to this as a factor.

Williams (9), who installed weather instruments on several mountain lookouts in California from 1913 to 1915, stated that the records were taken every three hours. These included wind direction and velocity. In his report we find these prophetic remarks:

"The diurnal range in temperature in the mountains is considerable, and it is well known that at night, when the temperature approximates the dew-point and the relative humidity is high, forest fires lose much of their energy . . . The condition of the humus (duff) on the forest floor is a matter of vital import. No serious fire may be expected until after it has become dry."

He considered drying winds and very warm weather the two most potent causes and he noted, "A north or northeast wind causes a decided drop in humidity in California, and a rapid drying of the forest floor . . . the reverse being true of the west wind. . . Low pressure and low humidity accelerate evaporation." Williams has, therefore, definitely pointed to the influence of moist air on lowered inflammability on the forest floor.

Palmer (7), commenting on the unfortunate forest fires situation in California stated:

"The fire-weather warning service was inaugurated in the Pacific Coast states in 1913 on the recommendation of the district forecaster E. A. Beals . . . Zones of marked hazards from lightning are due partly from mineral deposits, soil variations, and altitude. Drouth is a prerequisite of a forest fire, high winds, partly because they accelerate evaporation, but principally because of their fanning effects, are second only to drouth as a contributing factor. Hot northerly, desiccating winds,

characteristic of the front portion of an anticyclone, are the most troublesome predisposing cause of forest fires in California. During the summer months the weather of California is dominated by the great North Pacific High. For this reason the surface winds are local in origin while the upper air is almost stagnant as far as horizontal currents are concerned . . . . When anticyclonic conditions are well developed the resulting surface winds are from the north or northeast, the direction of the most dangerous fire-winds of the state. Partly because of their excessive dryness, but principally because of their fanning effect, these winds are the most dreaded by the foresters."

#### THE INFLUENCE OF CYCLONES AND ANTI-CYCLONES ON FIRE WEATHER IN THE PACIFIC NORTHWEST

The summer of 1919 became one of the worst in the northern Idaho fire history. With precipitation far below normal throughout July and August, there occurred several dangerous peaks of hot weather, greater than ordinary wind movement, and low daily relative humidities. Two such periods occurred in July and two in August. As the period July 11 to 20 progressed toward a climax, the thermometer registered an increase from day to day with a corresponding drop in the relative humidity for each afternoon. Records from August 10 to 19 show the same progression. During both of these periods the lowest humidity dropped to 10 per cent and marked the climax of a very serious fire situation.

The more complete record for Spokane, Washington, fifty miles to the west and on the eastern border of the Columbia Plateau, are given here in greater detail. They reveal for July and August, 1919, several unusual approaches of dangerous forest fire weather spanning periods of eight to ten days culminating in rather high wind and temperature and very low air humidity. The buildup from August 10 to 20 is given in Table 1.

TABLE 1  
WEATHER CONDITIONS AT SPOKANE, WASHINGTON, AUGUST, 1919

	Date										
	10	11	12	13	14	15	16	17	18*	19	20
Max. Air Temp.	88	91	86	76	81	81	88	92	95	89	88
Pressure (inches)	27.88	27.84	27.94	27.98	27.06	27.99	27.86	27.88	27.98	28.02	27.90
Rel. Hum. 5 P.M. (%) . . .	19	16	15	22	22	22	18	20	10	16	21
Wind Ave. (m.p.h.) . . . .	2.5	5.4	11.2	11.0	3.3	3.0	2.8	2.1	6.8	8.8	3.5
Wind Max. (m.p.h.) . . . . .	15	8	14	22	21	12	12	10	8	17	19
Wind (direction) . . . .	N	NW	SW	W	NE	NE	E	E	W	W	S
Cloudiness . . . . .	1-	5	4	7	1	1-	5	3	1	4	1-

\* August 18 and 19 were marked by very low humidity and high west winds. This was a period marked by many rapidly spreading forest fires.

In the summer of 1919, weather instruments were placed on four different mountain lookouts in northern Idaho with the idea of obtaining records of wind velocity and direction, air temperature, and relative humidity, in order to correlate these with forest fires in the region (Larsen, 3). Some of the conclusions are as follows:

"The data obtained revealed that in Idaho the westerly winds carried in drier air than the easterly. This was the reverse of observations in California and Oregon. The explanation is that the west winds in Idaho traversed the treeless and partly barren Columbia Plateau and the Snake River Valley where low humidity and scant precipitation occur in summer. The easterlies from Montana passed over more uniformly forest-covered land and areas which register higher summer humidity readings. The monthly minimum relative humidity readings give 20 per cent for the Intermountain area and 25 per cent for Spokane, but 40 per cent for Miles City in eastern Montana. Humidities at Portland, Oregon, and other points west of the Cascade Range also record higher values than anywhere in the Intermountain region.

This study revealed further that temperature and humidity fluctuate less at the high stations than low ones in the same territory, and that the danger from high winds in the elevated mountain areas is greatly counteracted by an increase in the atmospheric humidity. Critical conditions are reached in the lower valleys on warm, sunny days occasioned by low humidity and high winds. Many forest fires which rage unabated on lower slopes have been observed to slow down and become easily controlled at higher elevations.

It should not escape our attention that all of these men who hitherto had given thought and study to the fire situation fully realized that winds coming from the north and northeast toward California brought high temperatures and low humidity. In Idaho, on the other hand, winds blowing from the west and southwest brought about the most critical fire conditions.

#### ASSISTANCE REQUESTED

In 1916 the appeal went out to the United States Forest Experiment Stations to begin studies on these problems, and the following suggestions for approach were made:

- A. Division of the nation's forest regions into climatic units, on the basis of differences in air temperature, precipitation, forest types, etc.
- B. Study of the possibility of predicting the approach of danger conditions by the use of one or more easily obtainable factor, moisture of surface litter, etc.
- C. Collection in all districts of adequate meteorological data for use in fire protection and fire studies.
- D. Study of weather conditions which are dangerous and the possibility of predicting such conditions.
- E. The relation of local climatic phenomena, such as winds, etc., to regional conditions.

F. The rate of spread of fires under various conditions of weather, topography, and cover.

The Washington office also recommended the division of the large regional forest areas into smaller climatic units, as a necessary preliminary to much of the other fire studies, stating:

"It will probably be found that the seasonal variations of the climatic factors is a more important guide than the total quantities . . . . Care should also be exercised in allowing for different elevations and forest types . . . . It will be necessary to pick out some one very simple factor, resultant of all the climatic factors which influence hazard, and determine the relationship of the resultant factors in the various forest types of a given climatic region, (unit). A factor suggested is moisture of surface litter which is a resultant of precipitation, temperature, humidity, evaporation, and wind movement. When samples are taken, inflammability tests can be made. The correlation of forest fires and weather records involves the parallel study of fires and weather records for definite localities in order to determine which of the predictable climatic phenomena has a direct relation to fire danger or indicates a means of predicting such relations. The rate of spread of fires must deal with variations in forest cover, topography, and weather."

Clearly, there could be no doubt but that these statements referred in some measure to the articles from Beals, Williams, and Munns.

The following additional notes arrived later from the Washington office, classifying destructible resources as follows:

1. Merchantable timber; 2, immature timber and reproduction; 3, forage; 4, watershed values; 5, improvements by man; 6, soil values; 7, recreation values. The factors which affected the spread of fires were considered as: A. Inflammability, which included topography, forest cover and ground cover; B. Climate; C. Control ability, which in addition to A included accessibility; and D. Safety, embracing available manpower, food supplies, transportation facilities, etc.

Pursuant with the above requests and suggestions, studies were begun by S. B. Show (8) in California, and J. A. Larsen (4) in Idaho. Munns (6) had already begun correlation work in southern California. To the best of the author's knowledge no studies in these lines were undertaken at the other western forest experiment stations or districts. The author asked the director of the Wind River Station in 1919 what had been done in fire-weather studies in Washington and Oregon. The answer was, "Not a thing."

The studies made by Munns (6) embrace correlation of vapor pressure, evaporation, and fire danger. He obtained weather records at the Converse Forest Experiment Station at 6,000 feet elevation in the San Bernardino Mountains, California, for 1915 and 1916. The vapor pressure data were gathered at various Weather Bureau stations in California. At the outset Munns stated that evaporation was the resultant of air temperature, wind, and relative humidity; that each one of these was able to increase the rate of evaporation, either by their single or

combined influence; that with an increase in the rate of evaporation the number of large fires increased and the size of the individual fire greatly augmented. When the rate of evaporation decreased the area burned was decidedly less. Munns said that the occurrence of fires and the rate of evaporation did not follow the course of relative humidity because the latter is a very changeable and unreliable factor except for the immediate period when it is determined, although it does follow temperature in its general trend.

In search for a meteorological factor which would permit correlations with fires, he came to the conclusion that there was enough correlation to make certain that vapor pressure was the big factor influencing evaporation, and therefore the spread of fires, and that the changes in the vapor pressure are more gradual than those of relative humidity. Attention was also invited to the fact that the periods during which the north and east winds occurred were those in which the largest fires and those most difficult to control were experienced. These are essentially desert winds coming from the arid Intermountain region of the West. They occasion rapid evaporation and a rapid spread of fires.

In response to the request for studies of the regional climatic units, Larsen and Delavan (5) made an exhaustive compilation and summary of all the forest fires and climatic records for Montana and northern Idaho from 1909 to 1919, inclusive. These set forth the total numbers of fires which had occurred within each of the seven subregions in that decade, with records of precipitation for safe and for critical seasons, the areas burned and the associated air temperatures, precipitation, wind, and relative humidities.

In 1910, a summer marked by the very worst fire season, the precipitation deficits began in May and continued with increasing departures below the normal for June, July, and August. Another contributing cause was the early disappearance of snow in the mountains.

From 1909 to 1919 there were about 10,000 national forest fires in Idaho, north of the Salmon River, and the state of Montana combined. Of these the Idaho section had 5,116 fires, and the very much larger territory of Montana, 4,813 fires. On the basis of the areas burned per 100,000 acres the Idaho units had 68,478 acres burned, and the Northwest Montana forests had 19,332 acres burned. The other more easterly Montana units showed areas from 1,000 to 8,000 acres burned per 100,000 units.

#### CORRELATION OF FIRE-WEATHER, DUFF MOISTURE AND INFLAMMABILITY

Show (8), in 1919 focused his attention on the ignition point of the needle duff on the forest floor, the seasonal march of the evaporation, and the rate of spread of surface fires under varying wind velocities. He stated that the ignition point of the duff was reached when its moisture content went below 8 per cent of its dry weight, and that the flame would then continue to spread. The moisture loss of the duff was very rapid under the summer sun, on southerly slopes, but much slower in the shade and on north aspects. Wind, temperature, and evaporation culminated in

maxima each afternoon. Under conditions of zero wind movement the perimeter of the test area burned each five minute period was assumed as zero; with wind at one mile-per-hour the perimeter was 32 feet; with a four mile-an-hour rate it was 120 feet; with nine miles, 285 feet; and with twenty-five miles, 715 feet. Show concluded, therefore, that the rate of spread of the surface fires (at the beginning of a forest fire, before it began to travel through the crowns of the trees), varied as the square of the miles-per-hour of the wind movement.

In the course of these tests, although Show did not place special stress on the influence of relative humidity, he made the statement that air-dried litter had the property of taking up moisture from the air, chiefly at night, to the extent of from 5 to 6 per cent of its own weight. This means that an increase in the relative humidity of the air, which comes with a lowering of the temperature, imparts moisture to the duff because of its hygroscopicity and thereby lowers its inflammability.

At the Priest River Forest Experiment Station in northern Idaho, Larsen (4) began weather and forest fire studies with duff moisture determinations and ignition tests in 1916. An attempt was also made to correlate dangerous fire-weather conditions with general regional climatic variations, by noting the influence of high and low pressure areas which passed over the state from west to east. The following are condensed abstracts from the first progress report: It was found that the needle duff under the evergreen forest would not burn with a flame unless its moisture content went below 8 per cent of its dry weight; that this ignition point was reached sooner on exposed aspects than under the forest cover; that the rate of drying depends largely upon the climatic factors and the aspect, degree of exposure, amount of cover, etc., being most rapid on the southwest exposure. The greater the initial moisture content of the duff the steeper was the descending desiccation curve during the drying out period. In the weekly comparisons it was found that the amount of moisture in the duff samples fluctuated according to air temperature, sunshine, and evaporation. The wind increased with the rise of temperature during the day, but also on the approach of rain associated with the low pressure areas.

During the season of 1917, daily instead of weekly correlations were made of air temperature, relative humidity, wind, evaporation, and precipitation. It was found that the curves which showed duff moisture conditions also followed and lagged behind those of the relative humidity, but the drop in the duff moisture curves was very much steeper, though less fluctuating than those of the relative humidity. The descending duff moisture content curves went lower and lower each day subsequent to rain until they assumed a nearly horizontal position at their minimum values. However, these same curves rose again on the approach of cloudy weather and increase in the relative humidity of the air—even before rain had actually fallen. Here then, was a direct proof that moisture was absorbed and inflammability decreased by an increase in relative humidity of the atmosphere. Some of these relations are clearly shown by the data given in Table 2.



TABLE 2  
RELATIONS OF RELATIVE HUMIDITY AND DUFF MOISTURE, JUNE AND JULY, 1947

Period	Days	Precipitation (inches)	Relative Humidity 5 P.M. (percentage)	Duff Moisture (percentage)
6/23-6/26 . . . . .	3	0.87	63.0	64.4
6/26-6/27 . . . . .	1	0.0	26.0	34.4
6/27-7/2 . . . . .	5	0.0	62.0	14.1
7/2-7/5 . . . . .	3	0.0	39.0	10.2
7/5-7/9 . . . . .	4	0.0	39.0	15.7
7/9-7/12 . . . . .	3	0.0	25.0	8.3
7/12-7/16 . . . . .	4	0.0	24.0	10.0
7/16-7/19 . . . . .	3	0.0	35.0	1.5

In order to test more closely the ability of pine needle duff to absorb water vapor from the atmosphere hygroscopically, such samples were gathered from the forest floor, oven dried, and placed in wire baskets on the laboratory floor overnight in summer. The doors and windows of the building were left open to admit the night air. Thus there would be little danger of overnight increase in moisture from dew or rain. At 8 o'clock in the morning on several occasions the moist air had found its way to the duff in the baskets, which then gave an increase in weight over that of the previous evening. An increase was also observed in the relative humidity of the morning air within the building.

Burning tests were made of oven-dried duff both in dry and in moist atmosphere outside of the laboratory, and from these it was discovered that the height of the flame and the rate of consumption of the dry duff samples were identical in both dry and humid atmosphere. When, however, the duff samples began to absorb moisture from the damp air, as indicated by increase in weight, the rate of incineration and the height of the flame were reduced.

The difficulty attending the statistical correlations arising from the wide moisture fluctuations in duff from the forest floor has been overcome by H. T. Gisborne by the use of logarithmic paper and the use of standard samples of western yellow pine wood, which also possess hygroscopicity, but of a less fluctuating oscillation than needle duff.

#### SUMMARY

It may be stated that correlation of critical forest fire situations and weather conditions was the subject of study by several members of the United States Weather Bureau and research men at a few of the western forest experiment stations previous to 1920. These endeavors mark the beginning of such studies in the United States. Up to the year 1920 the following facts seemed fairly well established: Unusual and critical forest fire situations develop during prolonged periods of sub-

normal precipitation—especially from spring and leading into the mid-summer months; winters with scant snowfall, when followed by low spring rainfall, greatly intensify the hazard; periods of anticyclonic conditions produce dangerously dry winds when they travel from the Intermountain desert areas either toward the Cascade and Sierra ranges or toward the northern Rocky Mountain or Bitterroot ranges in Idaho; high temperatures and the associated low relative humidity connected with the anticyclonic movements produce rapid evaporation of moisture from the duff in the forest and a general increase in inflammability and rate of spread of forest fires. The great heat associated with large forest fires naturally lowers the atmospheric humidity, and creates strong wind which is no small factor, in fanning and spreading forest conflagration. (The evidence of long rows of unburned but broken trees pointing inward to the burned areas is a mute testimonial to the strong rush and force of the air toward large areas on fire.)

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## EVALUATION OF TREE RISK IN THE SPRUCE-FIR REGION OF THE NORTHEAST

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In attempting to find possible means of combating recurrent epidemics of the spruce budworm<sup>1</sup> in the Northeast, research has shown that forest management has considerable promise. Reduction in the proportion of balsam fir to spruce and attainment of the highest possible proportion of rapidly growing trees are expected to result in a less severe outbreak and a higher percentage of recovery following defoliation. These principles of silvicultural control have been discussed in detail by Graham and Orr (2), Balch (1), Westveld (5), and McLintock (3).

The recommended practice, now being tested on a large scale in the spruce-fir region, is a single tree selection system on as short a cutting cycle as possible—no longer than twenty-five years and preferably fifteen or twenty, or even shorter if feasible. This, of course, means marking the trees to be cut, and requires a considerable degree of care and skill in selecting the trees to be left for the next cut. Thus the need for a simple tree classification to enable rapid ocular evaluation of relative "risk" of spruce and fir of different size, age, and condition becomes immediately evident. While in many cases decision to cut or leave a tree will be clearly indicated by its size, presence of defect or damage, overmaturity, etc., there are as many borderline cases where more careful consideration of the factors that influence growth is called for.

An early attempt at such a classification was made on the basis of vigor as expressed by external features that were indicators of vigor, or growth rate, in the tree. Thus, a Vigor I spruce or fir has a dense, well developed crown, usually—but not necessarily—symmetrical, with foliage and bark color typical of a healthy tree. It shows no evidence of disease or other damage and is making rapid lateral and terminal growth. Vigor II trees are usually of two types; those of good form and in apparently healthy condition, but making considerably less terminal and lateral twig growth than the Vigor I; and those making good twig growth, but having rather thin, poorly developed or one-sided crowns. Vigor III trees are those with markedly poor crowns, whether because

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<sup>1</sup>The spruce budworm (*Archips fumiferana* Clem.) is a defoliator, feeding principally upon balsam fir (*Abies balsamea* Mill.), white spruce (*Picea glauca* Moench), and red spruce (*P. rubens* Sarg.). Epidemics seem to run in 30- or 35-year cycles, the last outbreak having been between 1910 and 1920. At that time, stumpage conservatively estimated at 100 million dollars was destroyed in Maine alone. The current outbreak now devastating the forests of Eastern Canada again threatens the Northeast.

of slow terminal growth, overmaturity, sparse or yellowing foliage, trunk or crown deformity or damage, or any other physical manifestations of an unhealthy or dying tree.

Arbitrary limits of diameter growth for five- and ten-year periods believed to coincide with these vigor classes were established, following examination of about 1,800 spruce and fir increment cores (Westveld, 4). Field checks were then carried out to determine the actual degree of correlation between appraised vigor and actual growth. It soon became apparent that one or two other factors often exerted more influence upon growth than the characteristics of vigor enumerated above. For example, since spruce and fir are both tolerant species, a tree with all the features of a Vigor I but intermediate in crown class frequently had the growth rate of a Vigor II. Similarly, a dominant or co-dominant with a high crown ratio often made diameter growth typical of a Vigor I, although appraisal on the basis of external characteristics made it Vigor II. It was observed that the vigor characteristics were most dependable when applied to trees up to the point of maturity. As the trees reach maturity, the appearance of bark and foliage becomes less reliable as an index of growth. At the same time, the position of the tree in relation to sunlight (crown class) and the relative extent of its food manufacturing plant (crown ratio) exerted more influence upon growth.

Growth records confirmed the basic assumption that in general, on a given site, growth rate varies directly with the level of vigor, crown class, and crown ratio. Table 1 presents five-year diameter growth averages measured on increment cores taken from 188 balsam fir and 300 spruce, classified according to the three criteria mentioned. For

TABLE 1  
FIVE-YEAR DIAMETER GROWTH FOR SPRUCE AND FIR, AVERAGE FOR CROWN CLASS, VIGOR, AND CROWN RATIO

Item	Red Spruce (Inches)	Balsam Fir (Inches)
Crown ratio:		
High (7-10) .....	0.70	0.76
Medium (4-6) .....	.52	.60
Light (1-3) .....	.33	.39
Vigor:		
I .....	.59	.72
II .....	.51	.50
III .....	.33	.40
Crown class:		
Dominant and co-dominant .....	.58	.68
Intermediate .....	.43	.49
Overtopped .....	.36	.37

convenience, crown ratio has been expressed in whole numbers rather than per cent (i.e., crown ratio of 4 means length of living crown is 40 per cent of the total tree height), and has been divided into three levels, as indicated in the table.

However, in practice the concept of *relative* growth rate is associated with interactions of different crown classes with different levels of vigor, and with interactions of both of these with varying degrees of crown ratio. No one of the three taken individually provides as reliable an estimate of relative growth rate as all three considered as a complex. To permit evaluation of the relative rate of growth of two adjacent trees to determine which is the better risk, the combined values of the three must be considered. Thus in Table 2, diameter growth averages have been refined to represent each factor in terms of the other, and at each level.

TABLE 2  
FIVE-YEAR DIAMETER GROWTH FOR SPRUCE AND FIR, SHOWING INTERACTION OF CROWN CLASS, VIGOR, AND CROWN RATIO

Vigor and Crown Ratio	Crown Class					
	Red Spruce			Balsam Fir		
	Dominant and Co- Dominant (Inches)	Inter- mediate (Inches)	Over- Topped (Inches)	Dominant and Co-Dominant (Inches)	Inter- mediate (Inches)	Over- Topped (Inches)
Vigor I:						
CR 7-10. . . . .	.73	.64	.76	.86	.60	*
CR 4-6. . . . .	.61	.56	.38	.71	.57	.55
CR 1-3. . . . .	.51	.24		.51		
Vigor II:						
CR 7-10. . . . .	.67			.65		
CR 4-6. . . . .	.58	.41	.34	.58	.53	.37
CR 1-3. . . . .	.44	.39	.33	.55	.46	.24
Vigor III:						
CR 7-10. . . . .						
CR 4-6. . . . .	.60	.24	.15	.59	.37	
CR 1-3. . . . .	.30	.14	.14		.14	.12

\* Blanks indicate fewer than four sample trees.

The limited scope of the data, however, and the fact that no provision has been made for differences in growing sites, do not allow literal interpretation of the growth averages. The means can be accepted and used in a relative sense only, and not as indices of absolute growth. This does not constitute a weakness in the present summary as only a relative evaluation is desired. The alignment of growth averages in both Tables 1 and 2 merely confirms the original hypothesis that a dominant tree is generally a better risk than an intermediate, a Vigor III a poorer risk than a Vigor II, and so on.

It now remains to simplify this scale one step further to provide a rule quickly and easily applied in the field by the man with the marking ax or paint gun. At the present stage of our knowledge, it must be assumed that an equal influence upon growth is represented by the three variables: vigor, crown class, and crown ratio. Thus we may say that on the same site a Vigor III fir, intermediate in crown class, and with a crown ratio of 7, can be expected to have approximately the same

growth rate as a Vigor I fir, overtopped, and with a crown ratio of 4. In other words, corresponding levels of each variable express the same relative growth rate. A simple "rating" system may be set up by which a tree is given from one to three "points" for its position in the scale of each of the variables, as follows:

Variable	Rating in points		
	3	2	1
Crown class .....	D. and co-d.	Intermediate	Overtopped
Crown ratio .....	7-10	4-6	1-3
Vigor .....	I	II	III

The first tree mentioned above would be rated one point for vigor, two points for crown class, and three for crown ratio, a total of six. The second tree would be rated three for vigor, one for crown class, and two for crown ratio, again a total of six.

With this as a basis, all growth measurements were pooled for spruce and for fir, and each tree was rated according to the system just described. Then mean diameter growth was calculated by species for each numerical rating. The results are shown in Table 3.

TABLE 3  
FIVE-YEAR DIAMETER GROWTH FOR SPRUCE AND FIR, BASED ON COMPOSITE RATING OF CROWN CLASS, VIGOR, AND CROWN RATIO

Numerical Rating	Balsam Fir		Spruce	
	Number of Trees	Mean Growth (Inches)	Number of Trees	Mean Growth (Inches)
9.....	21	0.86	17	0.73
8.....	56	.70	75	.62
7.....	43	.59	88	.59
6.....	31	.55	62	.44
5.....	25	.42	43	.31
4.....	7	.17	11	.19
3.....	5	.12	4	.14

It is again emphasized that a high degree of accuracy is not claimed for this rating scale, but it serves the purpose for which it was intended: to permit on a given site *relative* evaluation of tree risk, as expressed by growth rate, by means of three easily estimated variables. It is a working tool and guide for practicing foresters, timberland owners, and others who have occasion to mark spruce and fir for selective cutting.

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# DIAMETER-GROWTH STUDIES OF NORTHERN RED OAK AND THEIR POSSIBLE SILVICULTURAL IMPLICATIONS

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If some natural catastrophe suddenly befell all of the northern red oak *Quercus borealis* Michx. f. in southwestern Wisconsin, the total forest volume in most localities would be reduced by 60 to 80 per cent. No other timber species occupies a place of greater importance in the typical farm wood lot. This being the case, the many owners of small blocks of timber in the region usually are quite surprised to learn that comparatively little is known about the ecology or silvicultural management of the oak forest type.

A farm forestry research program under way in Wisconsin, Minnesota, Iowa, and elsewhere eventually should provide a sound basis for handling the extensive oak forests of the region. Pending the availability of data from controlled cuttings, foresters should not overlook the possibility of obtaining empirical information which may throw some light on this problem.

Some observations of this character, entailing a study of the diameter-growth rates of northern red oak in four widely-separated stands of good density, are the basis for this paper. In three cases the measurements were taken on stumps concurrently with logging. In the fourth instance the data represent changes which have occurred on permanent sample plots over a fifteen-year period.

The general objective of the study was to compare the diameter increment rates for northern red oak when this species occurred: (1) as single stems or small groups of trees in mixture with other more tolerant hardwoods, (2) as pure, or nearly pure stands of seedling or seedling-sprout origin, and (3) as pure, or nearly pure, stands of coppice origin. Some interesting differences were found which form the basis for the tentative conclusions presented here.

## PAST RECOMMENDATIONS FOR CUTTING OAK STANDS

A survey of the literature shows that the recommended cutting practice for the oak forest type usually is the shelterwood system or some modification of it (5, 6). Korstian (6) suggests, however, that the older trees in uneven-aged oak stands should be removed, individually or in groups by selection cuttings. Locke, too, (7) favors the group selection cutting method as the one most likely to stimulate satisfactory regeneration of oak seedlings. Other foresters (3, 4, 8) recognizing both its intolerance and its aggressiveness feel that the key to managing northern

red oak successfully may be clear cutting in narrow strips or small blocks. Under New England conditions, Lutz and Cline (8) found that even when all young hardwoods forming the understory of old-field white pine stands were cut back to the ground to provide a uniform canopy of seedling-sprouts, northern red oak often assumed wolf-tree characteristics in a relatively short period after the pine overstory was removed.

It is evident that there is no general agreement with regard to the best silvicultural system for managing the oak forest type. The dual objectives of management are, of course, production of the maximum increment of high-quality wood (1) and the establishment of a sufficient number of oak seedlings and seedling sprouts to perpetuate the species (2).

#### COMPOSITION AND VOLUME OF OAK-NORTHERN HARDWOODS TRANSITION TYPE

In the region in question the mixed-oak type ordinarily occurs as nearly pure even-aged stands. There is one forest type, however, comprising a mixture of northern hardwood and central hardwood tree species which contains considerable northern red oak of an uneven-aged character. As may be seen from Table 1, sugar maple (*Acer saccharum* Marsh) occupies the dominant place in this association. American bass-

TABLE 1  
COMPOSITION AND GROSS VOLUME OF UNDISTURBED MIXED-HARDWOOD STANDS,  
SOUTHWESTERN WISCONSIN

Species	Stand A*		Stand B†	
	Bd. Ft. per Acre (Scribner)	Percentage of Total Volume	Bd. Ft. per Acre (Scribner)	Percentage of Total Volume
Sugar Maple .....	6,395	68.5	4,669	53.6
Northern Red Oak	901	9.6	2,310	26.6
American Basswood	1,638	17.5	380	4.4
White Ash .....	176	1.9	379	4.4
Slippery Elm ....	138	1.5	299	3.4
Other .....	92‡	1.0	663§	7.6
Total .....	9,340	100.0	8,700	100.0

\* Location: Crawford County; Area: 80 Acres. Total basal area per acre, 106 square feet; average D.B.H. of sawtimber stand: 14.8 inches.

† Location: Vernon County; Area: 52 Acres. Total basal area per acre, 97 square feet; average D.B.H. of sawtimber stand: 13.9 inches.

‡ Butternut and white oak.

§ Butternut, white oak, hickory, red maple, bigtooth aspen, birch, and black cherry.

wood *Tilia americana* L.; white ash *Fraxinus americana* L.; slippery elm *Ulmus fulva* Michx.; white oak *Quercus alba* L.; butternut *Juglans cinerea* L.; red maple *Acer rubrum* L.; hickory *Carya cordiformis* (Wangenh.) K. Koch; *C. ovata* (Mill) K. Koch; bigtooth aspen *Populus grandidentata* Michx.; paper birch *Betula papyrifera* Marsh.; yellow

birch *B. lutea* Michx. f.; and black cherry *Prunus serotina* Ehrh. account for the remainder of the volume.

If stands such as these are to be managed by the selection system of cutting, they will tend to become even more uneven-aged. This means that some of the northern red oak will be subjected to crowding and partial overtopping at least for short periods. Similarly, upon being released, these trees must be able to recover quickly and grow at a normal rate.

Of the species within this transition type, northern red oak usually is considered one of the least tolerant. However, its presence in mixture with shade-enduring sugar maple, American basswood, and slippery elm suggests that this particular species of oak can develop into trees of sawtimber size under conditions of considerable crowding so long as it is not permanently overtopped.

#### ABILITY TO WITHSTAND OR RECOVER FROM CROWDING OR INTERMITTENT SUPPRESSION

In 1943 Stand A (Table 1) was logged by a clear-cutting operation. This provided an opportunity to obtain total age and radial growth for some fifty-two northern red oak stumps. The weighted age of the trees represented by these stumps was 96 years. Upon this basis, their total mean age was estimated at 100 years. Subsequent site index determinations showed that the oak had developed under conditions of average productivity.

Twenty-eight  $\frac{1}{5}$ -acre permanent plots were established on Tract A prior to the time it was logged. A tally of the merchantable (9.6 inches d.b.h. and larger) northern red oak on these sample areas shows that they averaged 13.8 inches d.b.h. This compares very favorably with the 14.1-inch average for co-dominant and dominant trees in full-density, 100-year old, even-aged oak forests on sites of average quality (4). This may or may not be merely a coincidence. It does lead to speculation, though, as to whether the annual diameter growth of northern red oak on a specified site may not average about the same over a rotation as long as 100 years regardless of whether the species occurs in pure, even-aged stands or as scattered, variable-aged stems in mixture with other hardwoods. Much more information will be needed to establish this point which obviously is very important silviculturally.

One thing brought out in the analysis of the fifty-two northern red oak stumps is the apparent ability of this species to withstand prolonged crowding and subsequently to recover and grow at an accelerated rate (Table 2). Despite the occurrence of the oak as three distinct, although somewhat broad, age classes, the improvement of growing space with time is clearly evident in each case. Even the oldest trees, averaging 141 years in age, more than doubled their diameter growth rates during the last 50-year period prior to logging. While no final conclusions can be drawn from a single series of measurements, the presence of such a wide variety of age and size classes does suggest the possibility of managing northern red oak under some form of selection

TABLE 2

MEAN AND PERIODIC ANNUAL DIAMETER GROWTH OF NORTHERN RED OAK IN AN UNDISTURBED MIXED-HARDWOOD STAND, SOUTHWESTERN WISCONSIN (STAND A)

Item	<i>General character of diameter growth during the entire life of the tree</i>		
	Above Average	Average	Below Average
1. Number of Trees.....	8	28	16
2. D.B.H.—Inches			
Average .....	11.6	15.5	17.2
Range .....	12.7–20.6	12.1–21.7	12.1–21.2
3. Total Age at 2-foot Stump Height			
Average .....	61	80	141
Range .....	41–70	73–87	117–168
4. Average Diameter of Stump, i.b.—Inches .....	15.2	15.7	17.1
5. Diameter Increment at a Stump Height of Two Feet* —Inches .....			
Mean annual .....	.217	.191	.122
Average Annual by Periods of Approximately Equal Length†			
Early period .....	.106	.090	.057
Middle period .....	.312	.209	.087
Final period .....	.301	.252	.209
6. Relative Annual Diameter Growth, by Periods, at a Stump Height of Two Feet—Percentage			
Early period .....	100	100	100
Middle period .....	323	232	153
Final period .....	287	280	367

\* According to Technical Note 198-C, Lake States Forest Experiment Station, University Farm, St. Paul 1, Minnesota, the growth rates at breast height would be about 92 per cent of the d.i.b. values at a 2-foot stump height.

† The length of the early, middle, and final periods, respectively were: For the eight "above average" trees—21, 20, and 20 years; for the twenty-eight "average" trees—20, 30, and 30 years; for the sixteen "below average" trees—41, 50, and 50 years.

cutting. This premise will be explored further by studies of Stand B, one of the Timber Harvest Forests which currently are being set up for demonstration purposes by the State of Wisconsin. Fifty-three permanent,  $\frac{1}{5}$ -acre sample plots have been established on this 52-acre mixed hardwood area. The past development of northern red oak and its response to various cutting intensities will be investigated in considerable detail as this tract is progressively logged.

#### DIAMETER GROWTH IN PURE, EVEN-AGED STANDS OF GOOD DENSITY

While *Quercus borealis* apparently can attain merchantability under conditions of temporarily severe crowding, this fact alone cannot be taken as proof that the species should be managed by the selection system of cutting. The following considerations, especially, weigh heavily

against such a conclusion: (1) the majority of the present-day oak wood lots, which came in more or less concurrently with early agricultural settlement, occur as nearly pure, even-aged forests, and (2) there is more chance that the regeneration of northern red oak will be adequate for restocking in stands whose overstory is comprised largely of oak than in those forest mixtures which run heavily to tolerant hardwoods, especially sugar maple.

Another argument in favor of managing mixed-oak forests by some cutting system which will result in an even-aged growing stock is the optimum character of diameter growth which occurs in such stands. The logging in 1944 of two oak sawtimber tracts of the foregoing description provided an opportunity to study diameter growth of eighty-seven northern red oak trees during the entire period of their development.

One of these wood lots, Stand C, located in La Crosse County, Wisconsin, was 85 years in total age (82 years at a stump height of 2 feet), had approximately 90 per cent of full density, was on a very good site, had an estimated gross volume of 18,000 board feet per acre, and was practically pure *Q. borealis*. The second tract, (Stand D) located in Sauk County, Wisconsin, was 100 years old (96 years at a 2-foot stump height), had roughly 95 per cent normal stocking, grew on a site of good quality, and had an estimated volume of 16,000 board feet per acre. It consisted of a mixture which in terms of sawtimber volume was 73 per cent northern red oak, 14 per cent bigtooth aspen, and 13 per cent red maple, American basswood, slippery elm, and white oak. Multiple stems were rare in both stands, indicating that they were of seedling or seedling-sprout origin. The quality of timber from the two tracts was exceptionally high. Veneer logs comprised 53 per cent of the total merchantable volume in Stand C, and 44 per cent in Stand D.

A summary of the average annual growth in diameter of *Q. borealis* in these two mixed-oak stands is presented in Table 3. Probably the most significant point brought out by this table is the fact that the average annual diameter growth rate during the early period, the length of which was about one-third of the total age of the stands at the time they were cut, was not strikingly different than the rates during the second period of their development. In other words, the individual stems of the overstory suffered very little initial crowding. Another point of interest brought out by diameter-growth analysis is that the crown classes which the trees occupied at the time they were felled were probably the same ones they occupied during early life. This suggests that northern red oak asserts and maintains its dominance almost from the late-seedling or early-sapling stage.

In order to duplicate tracts C and D silviculturally, it would be necessary to establish 1,200 to 1,350 seedlings or seedling-sprouts per acre during the ten-year period prior to the final cut. This assumes an initial stocking of about 75 per cent normal (4). The exact cultural treatment which will accomplish this goal is, of course, a moot question. However, it seems that the ultimate choice most likely will be either the shelterwood system, or clear cutting in very narrow strips or by small blocks. In case the shelterwood system is used, the data presented

TABLE 3  
AVERAGE ANNUAL DIAMETER GROWTH AT STUMP HEIGHT, BY PERIODS,\* FOR NORTHERN RED OAK IN TWO EVEN-AGED, WELL-STOCKED MIXED-OAK STANDS, SOUTHWESTERN WISCONSIN

Diameter of Stumps, i. b., Inches		Approximate Crown Class	No. of Trees	Diameter Growth at a Stump Height of 2 feet†						
Range	Average			Mean (inches)	Early Period (inches)	Middle Period (inches)	Final Period (inches)	Early Period (%)	Middle Period (%)	Final Period (%)
Stand C‡										
10-14	13.4	Suppressed	9	.163	.176	.198	.123	100	112	70
15-18	16.4	Intermediate	16	.200	.228	.211	.167	100	93	73
19-30	21.8	Co-dominant & dominant	17	.265	.290	.291	.219	100	101	76
Total			42							
Stand D§										
10-14	13.1	Suppressed	8	.138	.129	.130	.157	100	101	122
15-18	16.7	Intermediate	15	.176	.169	.185	.162	100	109	96
19-30	22.5	Co-dominant & dominant	22	.233	.209	.251	.233	100	122	111
Total			45							

\* The length of the early, middle, and final periods, respectively, for the two stands was: Stand C—30, 25, and 27 years; Stand D—30, 35, and 31 years.

† Diameter growth at d.b.h. is approximately 92 per cent of the rate at a stump height of 2 feet.

‡ La Crosse County. (Average age: 82 years).

§ Sauk County. (Average age: 96 years).

in Table 3 seems to indicate that the initial cuttings should be thinnings-from-below which take out the slower-growing and smaller-crowned suppressed and intermediate stems. This would leave the most vigorous trees for producing seed, put the accelerated increment on the top-quality stems, and maintain sufficient crown density to check the invasion by woody shrubs and reproduction of unwanted tree species.

#### GROWTH OF NORTHERN RED OAK IN SECOND-GROWTH COPPICE STANDS

Clear cutting in narrow belts or by small blocks may prove to be one of the most effective methods for perpetuating mixed-oak forests. However, if this silvicultural system is used, coppice regeneration should be discouraged and seedling and seedling-sprout reproduction encouraged as much as possible.

This conclusion is based on diameter measurements of twenty 1/10-acre, permanent sample plots established in 1932 on a timbered watershed within the boundaries of the Upper Mississippi Valley Soil Conservation Experiment Station farm near La Crosse, Wisconsin. The history of this tract is somewhat obscure. At the time the plots were laid out, the forest cover consisted mainly of multiple-stemmed northern red oak, clearly of coppice origin. When the original field measurements were taken in 1932, the average age of the dominant stand was forty years.

TABLE 4

COMPOSITION, AVERAGE DIAMETER, MORTALITY, AND GROWTH OF A 40-YEAR-OLD MIXED-OAK STAND, LACROSSE COUNTY, WISCONSIN

Species	Av. D.B.H. of All Trees		Total Basal Area per Acre			
	1932	1947	1932	Mortality (1932-1947)	Present Growing Stock	
					1932	1947
	(in.)	(in.)	(sq. ft.)	(sq. ft.)	(sq. ft.)	(sq. ft.)
Northern red oak	6.5	8.1	61.931	5.127	59.804	86.697
Bigtooth aspen	9.2	10.5	11.937	8.787*	2.250	3.639
Paper birch . . .	1.9	5.7	5.119	2.684	2.435	2.919
White oak . . .	4.3	5.1	1.771	1.132	3.639	1.681
Black walnut . . .	1.1	6.1	2.867	0.099	2.768	1.196
Hickory† . . . .	3.0	3.6	1.210	0.131	0.809	0.992
Miscellaneous‡ . .	2.1	4.7	0.580	0.092	0.488	1.504
Average . . . . .	5.8	7.6				
Total . . . . .			90.515	18.352	72.193	104.268§

\* Of this total 0.153 square feet was mortality and the balance of 8.634 square feet was the 1932 basal area of 13 trees which were cut in 1944. At that time they had added 2.386 square feet of new growth.

† Shagbark and bitternut hickory.

‡ American elm *Ulmus americana* L.; boxelder *Acer negundo* L. and butternut.

§ This does not include 0.228 square feet of in-growth consisting of 9 paper birch, 4 black walnut, 2 butternut, 2 bigtooth aspen, 1 boxelder, and 1 white oak.



Prior to that date, the tract had apparently been pastured heavily for many years; livestock have been excluded during the past fifteen years. Field determinations made in 1937 indicated that the site was of average quality.

Table 4 shows the composition and total basal area per acre of the tract in 1932 and 1947. In terms of total square feet per acre for all species the stand was 96 per cent normal in 1932 and 94 per cent in 1947. The latter percentage figure would have been somewhat higher except for a minor logging operation which removed 13 mature, bigtooth aspen in 1944. The basal area of these trees at the time they were cut amounted to 11 square feet.

The growth made by the La Crosse, Wisconsin, series of plots has not been particularly encouraging (Table 5). It is evident that the average diameter increment during the past fifteen years is only 49 to 55 per cent that of the mean rate during the first forty years in the life of the stand. Seemingly this northern red oak coppice has lost much of its early vigor at a period when stands of seedling or seedling-sprout origin are making their best diameter growth (*see* data for stands *C* and *D*, Table 3). Here again a single set of observations admittedly is not an

TABLE 5  
DIAMETER GROWTH SUMMARY FOR NORTHERN RED OAK

No. of trees	Approximate crown class* in 1932	D.B.H., i.b. in inches†		15-year increase in diam.  (inches)	Average annual diameter growth at D.B.H., i.b.	
		1932	1947		First 40 yrs.	Last 15 yrs
					(inches)	(inches)
29 . . .	Suppressed	3.07	3.70	0.63	.077	.042
89 . . . . .	Intermediate	5.52	6.64	1.12	.138	.075
80 . . . . .	Dominant and Co-dominant	8.40	9.94	1.54	.210	.103

\* Suppressed trees ranged from 1.6 to 4.5 inches d.b.h.; Intermediate trees ranged from 4.6 to 7.5 inches d.b.h.; and dominant and co-dominant trees ranged from 7.6 to 15.6 inches d.b.h.

† Obtained by Deter's (3) formula:  $D.B.H., o.b.$

$$\frac{1.115}{\dots}$$

adequate basis for any general conclusion. Nevertheless, the rapid falling off of diameter increment in the Upper Mississippi Valley Erosion Experiment Station stand does raise a question as to whether first- or second-generation coppice is a satisfactory growing-stock for producing thrifty, high-quality oak sawtimber. There is need now to broaden this study so as to include mixed-oak stands of sprout origin on a variety of sites.

#### SUMMARY

In four case studies, interesting variations were found in the diameter growth rates for northern red oak growing in southwestern Wisconsin. The analyses of the data form the basis for several tentative silvicultural conclusions.

1. Northern red oak can recover successfully from prolonged crowding and subsequently make satisfactory diameter growth in competition with such shade-enduring tree species as sugar maple, American basswood, and slippery elm. While limited observations cannot be taken as conclusive proof that *Quercus borealis* can be grown in variable-aged stands by selection cuttings, they do indicate that this species may have a higher degree of tolerance than commonly is supposed.

2. The typical mixed-oak farm wood lot of southwestern Wisconsin is even-aged and predominantly of seedling or seedling-sprout origin. Northern red oak is the most important single species in these stands.

An analysis of diameter growth in two mixed-oak tracts of good density show that *Q. borealis* developed under conditions of very little initial suppression. Furthermore, the trees comprising the overstory showed little tendency to shift from one crown class to another, which suggests that northern red oak asserts and maintains its dominance very early in life.

3. Clear cuttings which result in large blocks of even-aged coppice may be silviculturally undesirable for the mixed-oak forest type. Growth measurements carried on for a fifteen-year period in a tract of the foregoing character show that the early vigor of the sprout reproduction has declined by about 50 per cent, as measured by the average annual diameter increment, between the stand age of 40 and 55 years. Since this poor showing can in no way be attributed to overstocking, silvicultural cuttings of this type should not be recommended, at least on a large scale, until the growth of a number of wood lots of coppice origin can be studied in considerable detail.

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# PLANTING OF WATER-TOLERANT TREES ALONG MARGINS OF FLUCTUATING-LEVEL RESERVOIRS<sup>1</sup>

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Reservoir impoundments created for power, flood control, navigation, municipal water supply, or for general recreation have increased in number throughout the South during the last two decades. These reservoirs have extensive, sinuous margins that present certain land management problems that follow water-level management requirements. Questions arise as to the possible use of moderately or infrequently-inundated flats along reservoirs not adapted to cropping and pasture use. Forest planting is suggested as one solution on certain reservoir margins. Such plantations could, if successful, protect adjacent dike or road embankments during reservoir surcharge periods, provide cover and food for wildfowl, and produce a timber crop that would reduce management costs and benefit regional welfare.

The establishment of plantations along margins of fluctuating-level reservoirs presents problems. Expected limits and periods of water-level changes brought about by reservoir drawdown or surcharge must be known. Tree species must be adapted not only to existing soil types but also to changing water levels.

The Tennessee Valley Authority began establishing reservoir-margin plantings as early as 1935 on the lower Tennessee River. A study has been conducted to determine the initial development of water-tolerant trees planted five to twelve years on two kinds of reservoir-margin planting sites: 1, upper drawdown zones, consisting of bottomland soils intermittently covered by 1 to 3 feet of water at normal reservoir level through the growing season; and 2, reservoir surcharge zones, ranging from 1 to 15 feet above normal reservoir level and having soils of bottomland to upland types that are infrequently flooded, chiefly during the dormant season. Summarized in this report are the results for the following tree species: baldcypress, *Taxodium distichum*; tupelo, *Nyssa aquatica*; sweet or red gum, *Liquidambar styraciflua*; green ash, *Fraxinus pennsylvanica lanceolata*; water oak, *Quercus nigra*; willow oak, *Quercus phellos*; southern white cedar, *Chamaecyparis thyoides*; and sycamore, *Platanus occidentalis*.

## REVIEW OF LITERATURE

Review of source material shows little has been reported either on

<sup>1</sup>This is a contribution from the Tennessee Valley Authority, Division of Forestry Relations, prepared by T. H. Silker, Forester. Acknowledgment is given to other personnel of this division, including I. C. Burroughs and the late George S. Perry for their work with the reservoir-margin plantations covered in this study.

reforestation work with the species included in the present study or on planting along fluctuating-level reservoirs.

Southern white cedar is the only one of the eight species studied that is not native to the Tennessee River watershed. This tree, indigenous to the Atlantic and Gulf Coastal swamps from Maine to southern Mississippi, is described by Korstian (2) as best adapted to the edges of fresh-water swamps on swamp peat soils overlying a sandy subsoil. The best height growth for typical 9-year old natural stands observed by Korstian from Florida to Connecticut averaged 13.2 feet.

Minckler (4) reported 5-year results on a reforestation test including baldcypress and red gum on upland sites in East Tennessee. In mixed plantings on north slopes baldcypress showed average survival of 72 per cent, and total 5-year height growth of only 0.7 feet. Similar plantings of red gum had survival of 42 per cent, and total height growth of only 1.9 feet. His conclusions for planting on upland old-field sites are that baldcypress should not be considered, and that red gum should not be used in broomsedge cover because of the risk of rodent damage.

Growth of twelve tree species in natural stands in the Mississippi delta was studied by Paul and Marts (5). They considered willow oak second only to overcup, among oaks adapted to low, wet areas. Because of the variety of uses for its wood, they considered tupelo the best species, other than baldcypress, to favor on the permanently wet sites where it is found.

Turner (6) found that soil and topography influence the distribution and growth rate of bottomland hardwood and coniferous types in river overflow areas in Arkansas. He reports that loblolly pine develops best in small stream valleys where soils of recent wash have a loose surface layer over 3 feet deep and have a permeable subsoil with low colloid content. Of all the factors affecting the growth rate of pine, he considers those affecting available soil moisture the most important.

On the upper Mississippi River, Green (1) studied the effect of impoundment of water on native tree growth along a series of pools. He found most of the green ash killed after three years of continuous flooding to a depth of 4 feet.

#### THE PLANTINGS

Plantations established from 1935 through 1939 were set in the upper drawdown zone of TVA reservoirs on soils intermittently covered by 1 to 3 feet of water at normal pool level. Baldcypress and tupelo wildling stock pulled or dug locally was used to establish the first plantings on Wilson Reservoir.<sup>2</sup> Similar plantations were set out in 1937 on Pickwick Reservoir, but here nursery-grown stock was used. Additional plantings of baldcypress and southern white cedar in 1939 brought the total to 12.5 acres. All plantings were made on soils of the stream bottoms

<sup>2</sup> Plantations were established by the TVA Division of Health and Safety, with the Division of Forestry Relations cooperating, to find out whether tree shade would suppress aquatic vegetation that aids the development of the *Anopheles* mosquito, carrier of malaria.

and terraces derived mainly from limestone material or Gulf Coastal Plain sands.

Reservoir drawdown may leave these plantations 1 to 3 feet above pool level during parts of the dormant and growing seasons. Occasional reservoir surcharges have covered plantations with 7 feet of water for as many of thirty days during the growing season. The three tree species tested were thought to be the best adapted to soils and to artificial water levels simulating conditions where these three species are found naturally.

Beginning in 1942, plantations were established in a reservoir surcharge zone extending from 1 to 15 feet in elevation above the normal pool level of 359 feet. These plantings were designed to form protective belts adjacent to relocated highway, railroad and dike fills along the Kentucky Reservoir on the lower Tennessee River.<sup>3</sup> Sixteen tree species, thought to be adapted to pre-impoundment soil conditions and to post-impoundment reservoir-surge water levels, were used. A total of 1,055 acres of these protective plantations was established from Benton, Kentucky, to Clifton, Tennessee, from 1942 through 1946 on bottom and terrace soils washed from limestone, loess, and Gulf Coastal Plain sands.

These plantings have been only infrequently inundated by reservoir surcharge and then chiefly during the dormant season. Planting sites ranged from wet areas found along old stream beds and swamps to small dry areas on soils from which the topsoil had been stripped by borrow operations or sheet erosion. Most areas, as in Figure 1, were in pasture or crop use just prior to planting. Thus the planting was done in fields generally bare of all but annual or perennial weeds or pasture grasses. After planting, natural succession of plant communities that had been arrested by agricultural operations began to develop.

#### SAMPLE PROCEDURE

Plantings of water-tolerant trees were sampled to show tree response to two planting zones found on margins of fluctuating-level reservoirs. Measurements were taken to give a representative sampling of the establishment and initial development of eight tree species.

Surcharge zone plantings, ranging from 1 to 15 feet in elevation above normal reservoir level, were sampled to obtain data on survival and total height of dominant and co-dominant trees by soil series.<sup>4</sup> In addition, these samples were described as to soil erosion condition and stage of ground cover attained: 1, weed; 2, broomsedge, *Andropogon virginicus*; and 3, woody.

Plantings in the upper drawdown zone, on areas intermittently covered by 1 to 3 feet of water at normal reservoir level, were sampled

<sup>3</sup> Plantations were established by the TVA Division of Forestry Relations for the Design Division to keep wave action during reservoir surcharge periods from reaching dirt fills. The usual riprapping of such fills with rock was not considered feasible in this area.

<sup>4</sup> Soils identified from preliminary soil maps of the Kentucky Dam, Wilson Dam, and Pickwick Dam areas, USDA, Bureau Plant Industry, Soils, and Agricultural Engineering.

by 1/20-acre plots to obtain survival and total height growth of dominant and co-dominant trees by mapped soil series. Additional measurements were taken on tree diameters, and the number of 7-foot posts was estimated.

Observations were also made on injurious agents affecting the two types of plantings.

#### RESULTS IN THE SURCHARGE ZONE

The five-year development of plantations in the 1 to 15 foot surcharge zone is summarized in Tables 1 and 2. Results are discussed by 1, cover and soil conditions; 2, water-level conditions; and 3, response of the species: baldcypress, water oak, willow oak, green ash, red gum, tupelo, southern white cedar, and sycamore.

#### COVER AND SOILS

Five-year survival and height growth of eight species, planted on soils showing little or no erosion, is averaged by three ground cover stages in Table 1. This table includes results for plantation samples on terrace as well as bottomland soils.

TABLE 1

SURVIVAL AND HEIGHT, BY GROUND COVER CLASS, OF EIGHT TREE SPECIES IN 5-YEAR-OLD PLANTATIONS ON BOTTOM AND TERRACE SOILS ABOVE PREVAILING RESERVOIR LEVEL \*

Tree Species	Plantation Development by Ground Cover Attained (Survival Percentage)				Places Sampled
	Hydrophytic Weed	Broomsedge	Woody	All	Number
Baldcypress .....	80	73	86	75	16
Water oak .....	80	76	80	77	22
Willow oak .....	80	76	80	77	22
Green ash .....	96	88	95	90	32
Red gum .....	70	72	.	72	49
Tupelo† .....	61	59	.	61	12
Southern white cedar .....	.	11	.	11	6
Sycamore .....	..	87	..	87	2
(Height—Feet)					
Baldcypress .....	5.1	4.5	6.6	4.8	46
Water oak .....	5.5	4.6	7.4	5.0	22
Willow oak .....	6.5	5.4	8.3	5.9	22
Green ash .....	6.3	5.0	8.1	5.4	32
Red gum .....	6.5	4.8	..	5.3	49
Tupelo† .....	3.8	3.3	..	3.5	12
Southern white cedar .....	..	4.6	..	4.6	6
Sycamore .....	..	14.3	..	14.3	2

\* Includes only samples on soils showing little or no erosion. Twenty-nine samples on eroded soils excluded.

† Excluded from averages are tupelo plantations that were virtual failures on which survival could not be measured accurately. This results in more favorable averages for tupelo than the representative sampling of other species.



FIG. 1. In left center is typical area for planting of water-tolerant trees for protection of highway embankment. The floodwater on the planting chance is overflow from Blood River, February, 1942. Now, the Kentucky Reservoir maximum surcharge attains a level several feet higher than this. Plantations were established to protect the new highway fill that is raised several feet above the old roadbed.

Weed cover listed in Column 1 of Table 1 was found primarily on swampy areas and old stream beds holding overflow water during the first part of the growing season. This cover consisted chiefly of hydrophytic weeds with beggarticks predominating. Trees planted on these areas grew better than did those on broomsedge areas but not so well as those on areas developing woody cover. Much of the good tree growth on sites supporting hydrophytic weed cover can be attributed to higher water tables. The good growth on such sites also may be attributed to soils having a loose and deep surface layer and permeable subsoil (6).

Best plantation growth, Column 3 of Table 1, was found on areas developing a volunteer woody cover of boxelder, sycamore, red gum, and green ash in the five-year span since plantation establishment. These areas were found in old stream beds or flats adjacent to creek channels. They differed from hydrophytic weed sites in having better drainage that permitted germination and development of water-borne tree seeds.

Broomsedge cover listed in Column 2 of Table 1 was generally found on the higher bottomland and terrace soils. This cover varied from light,



scattered broomsedge and Johnson grass clumps to dense stands admixed with goldenrod. Light stands were generally found on soils having a compact subsoil and low inherent productivity rating. Poor plantation growth was made on such areas. Good tree growth was generally made on moist but well-drained soils supporting heavy stands of broomsedge or Johnson grass admixed with goldenrod.

Twenty-nine plantation samples in the upper part of the 15 foot surcharge zone were not included in Table 1, since they showed moderate to severe sheet erosion and were typical of upland planting-site conditions. Growth of red gum on nineteen of these samples shows a correlation with the succession of ground-cover types and confirms results from another study (4). Where the topsoil had been removed or lost as a result of erosion, micro-communities of xerophytic weeds and grasses such as three-awn grass, poverty danthonia, and buttonweed, developed. Here red gum height growth averaged only 3.6 feet after five growing seasons. Where typical broomsedge and mixed goldenrod developed, red gum averaged 5.1 feet in height after five years. Height growth of planted red gum on areas reverting to volunteer woody cover within five years averaged 6.5 feet.

Table 2 summarizes the five-year height growth of five species, on bottomland soils only, by soil series and land class. Tree growth, by comparison with the average for each species, was best on Shannon soils, with Hymon, Beechy, Lindside, and Melvin following in that order. With the exception of Beechy soils, this is in keeping with their agricultural productivity rating and land class. Beechy is the most poorly-drained member of the Shannon-Hymon-Ina-Beechy catena but the subsoil allows good penetration of roots (3). Where Beechy soils are forested, willow, baldcypress, and tupelo predominate in the permanently wet areas. In favorable years good field crops may be raised on cleared soils, but in wet seasons, crop failures are common. As a result of this weather hazard, the agricultural productivity rating for Beechy and other slowly-drained soils is low. However, the slow drainage condition is apparently beneficial to the water-tolerant trees planted.

Plantation samples were too sparse on Ennis, Huntington, and Waverly soils to give an adequate picture of tree growth response to soil type. Better tree growth was found on Huntington, Hymon, and Beechy silt loams than on fine sandy loams which have a lower productivity rating.

#### WATER LEVELS

To date, inherent soil moisture has affected plantation development in the 15-foot surcharge zone more than have surcharge levels. Reservoir surcharge reaching plantations has occurred chiefly during the dormant season. Surcharge water covering some planting areas 2 to 7 feet throughout most of the dormant season has caused no apparent damage.

Water-level management has kept pool level on Kentucky Reservoir near elevation 358 during most of the growing seasons. Plantations range from normal pool elevation of 359 feet to maximum surcharge level of

375 feet. Water has been held on only a small portion of the plantings for an extended period during the growing season. Baldcypress, tupelo, and red gum flooded by 2 to 4 feet of "trapped" water from April through June of the third growing season showed no apparent damage. No information is available as to the adaptability of water oak, willow oak, and

TABLE 2

HEIGHT GROWTH BY SOIL SERIES AND RATED LAND CLASS, OF FIVE TREE SPECIES IN FIVE-YEAR-OLD PLANTATIONS ON BOTTOMLAND SOILS IN THE SURCHARGE ZONE OF FLUCTUATING LEVEL RESERVOIRS ALONG THE TENNESSEE RIVER

Soil Series and Land Class	Bald- cypress	Water Oak	Willow Oak	Green Ash	Red Gum
	(Feet)	(Feet)	(Feet)	(Feet)	(Feet)
Shannon 1 . .	5.6	5.5	6.1	6.5	5.4
Hymon 1 . .	4.7	5.8	7.5	4.9	6.9
Ennis 1 . .	5.9	.	.	.	6.6
Huntington* 1 . .	.	4.2	4.1	.	3.8
Lindside 2 . .	5.0	4.4	5.3	5.8	5.3
Beechy 3 . .	4.9	5.5	6.2	6.6	5.2
Waverly 3 . .	4.6	.	.	5.4	.
Melvin 4 . .	4.6	4.2	4.5	4.3	5.2
All soils . . . . .	5.0	5.1	5.9	5.8	5.4
Sample basis— number . . . . .	37	19	19	23	37

\* Half of the Huntington samples were on fine sandy loam having a lower productivity rating.

sycamore to such surcharge levels. However, it is unlikely that the balance of the plantations will ever be subject to extended flooding during the growing season. Trees should continue showing favorable development as long as surcharge levels do not greatly exceed nor extend beyond those that have occurred during the first five growing seasons.

With the exception of the poorly-drained, compact soils such as Wolftever, better tree growth was made on swampy sites with hydrophytic weed cover than on the same soils with broomsedge or grass cover indicating drier sites.

#### SPECIES

Performance of eight species used in the surcharge zone plantations is discussed in this section.

*Baldcypress* has shown satisfactory average development of 75 per cent survival and a height growth of 4.8 feet. The poorest plantations were on terrace soils in the upper part of the surcharge zone where xerophytic weeds and broomsedge cover developed. The better baldcypress plantings were found chiefly on the lower bottomland sites where woody cover or hydrophytic weeds developed.

*Water oak* and *willow oak* have produced good stands on the average, with survivals of 77 per cent. Exceptions of poor plantations occurred on terrace soils that have either moderate sheet erosion or compact subsoils. Water oak averaged 5.0 feet in height. Willow oak made consistently better growth than water oak and was second only

to sycamore with an average height of 5.9 feet. Flats that are moderately inundated during the late fall and winter by reservoir surcharge appear desirable planting sites, especially where these two oaks are wanted to provide cover and food for game. Their small acorns are relished by ducks and make a valuable supplement to the diet of transient or wintering birds.

*Green ash* has shown excellent survival over the variety of surcharge zone sites sampled. The average survival of 90 per cent exceeded that of the seven other species. Height averaged 5.4 feet. One small plantation flooded with a foot of "trapped" water throughout most of the fifth growing season suffered considerable mortality. This would seem to support the observation by Green (1) cited earlier. Accordingly, this species appears suitable for planting only where inundation is occasional and of short duration.

*Red gum* has shown an average survival of 72 per cent and a total height growth of 5.3 feet. Growth was greatly affected by soil type. On bottomland silt loams of Shannon, Hymon, and Beechy, growth was better than on the fine sandy loams of these same soil series. Red gum developed very poorly on terrace soils such as Wolftever having a compact subsoil and low productivity rating.

*Tupelo* plantings developed well only in seepage areas or where the water table was close to the ground surface. Survival and height of the better plantations averaged 61 per cent and 3.5 feet, but fell off badly as the planting progressed to higher and drier zones. Survival of this tree was generally so low that only the successful portions of plantations could be sampled accurately.

*Southern white cedar* plantations established by planting wildlings showed very poor survival of 11 per cent, but the trees that survived attained an average height of 4.6 feet.<sup>5</sup> Planting stock was spindling and had very poor roots. Most of the wildlings turned brown within two weeks after planting, indicating excessive drying. Southern white cedar made its best growth on moist bottom soils of the type most favorable to cypress. Extensive use of this species may be limited because of the current difficulty in securing suitable planting stock at a reasonable cost.

*Sycamore* plantings were limited to terrace soils, such as Sequatchie and Humphreys, where gravel and chert deposits were concentrated. Plantings of this species (Figure 2) have shown very good survival and excellent height growth, averaging 14.3 feet.<sup>6</sup> This study does not provide information on the adaptability of this species to wetter sites or areas subject to moderate and intermittent flooding during the grow-

<sup>5</sup> Other wildlings of this species that were lined out, mulched, and shaded for a year in the Norris Nursery showed very low losses. This stock developed good fibrous root systems and well-balanced tops. Outplantings of these transplants resulted in excellent first-year survival.

<sup>6</sup> The two samples were on soils showing little or no erosion. Two plantings on sites suffering moderate sheet erosion averaged 6.3 feet in height after five growing seasons. Observations on six other reservoir-margin plantings that were unsuited for sampling in this study showed sycamore averaged 7 feet in height and 70 per cent survival after five years.



FIG. 2. Sycamore plantation after five growing seasons on Sequatchie fine sandy loam, a well-drained terrace soil, in the 15-foot zone above normal pool level, Kentucky Reservoir. Although naturally a fertile soil, the excellent growth is attributed in part to fertilizer treatment of the field while in pasture prior to planting.

ing season. It appears, however, that sycamore is a good species for planting on the drier terrace soils in the upper surcharge zone.

#### RESULTS IN THE UPPER DRAWDOWN ZONE

The development of older baldcypress, tupelo, and southern white cedar plantations in the upper drawdown zone is summarized in Table 3.

Reservoir management has covered these planting sites with 1 to 3 feet of water intermittently during the growing season. Results are discussed by 1, soils; 2, water levels; and 3, species response to prevailing conditions.

TABLE 3

DEVELOPMENT OF THREE TREE SPECIES IN OLDER PLANTATIONS ALONG THE TENNESSEE RIVER INUNDATED BY 1 TO 3 FEET OF WATER AT NORMAL RESERVOIR\* LEVEL, IN OCTOBER, 1947

Tree species	Age Since Planting	Survival	Height of Dominant Stand		Diameter at Breast Height	Total Post Yield Per Acre*	Sample Basis
			Total	Growth, Av. year			
	(years)	(percentage)	(feet)	(feet)	(inches)	(number)	(number)
Baldcypress....	12	89	21.6	1.8	3.3	210	2
Baldcypress....	11	96	22.3	2.0	3.5	113	13
Tupelo .....	12	88	21.6	1.8	2.3	45	4
Southern white cedar.....	9	58	22.1	2.5	2.3	..	1

\* Estimated in units of 7-foot posts to a 4-inch peeled top diameter.

#### SOILS

The soils on these areas were rated before reservoir impoundment as first or second class soils. Soil quality probably has not been a limiting factor to development of the plantings. Iuka fine sandy loam and Huntington silt loam predominate in the samples. Although these soils vary in agricultural productivity rating, no apparent difference in tree growth was noted between plantations located on them.

#### WATER LEVELS

An earlier examination of baldcypress and tupelo plantations on Wilson Reservoir, after six growing seasons, showed trees planted 3 feet above normal pool making only moderate growth even though survival was exceptionally good. Starting in 1943, reservoir management raised the normal lake level so that 1 to 3 feet of water intermittently covered the plantations during the growing season. Tree height growth increased after the water level was raised, and good annual growth has been maintained since that date.

Some plantings were flooded the first few growing seasons to a depth of 3 to 7 feet and for periods up to thirty days. An illustration of how prolonged flooding has set back some plantations is given in Figure 3. Here terminal shoots of the tupelo trees were killed by the prolonged flooding, but new sprouts developed after levels dropped and some trees now have 2 to 5 stems.

#### SPECIES

*Baldcypress* planted at spacings varying from 4 x 4 to 8 x 8 feet, has shown an average survival of 95 per cent after eleven years. One eleven-year planting at a 7 x 7 foot spacing averaged 30 feet in height. The

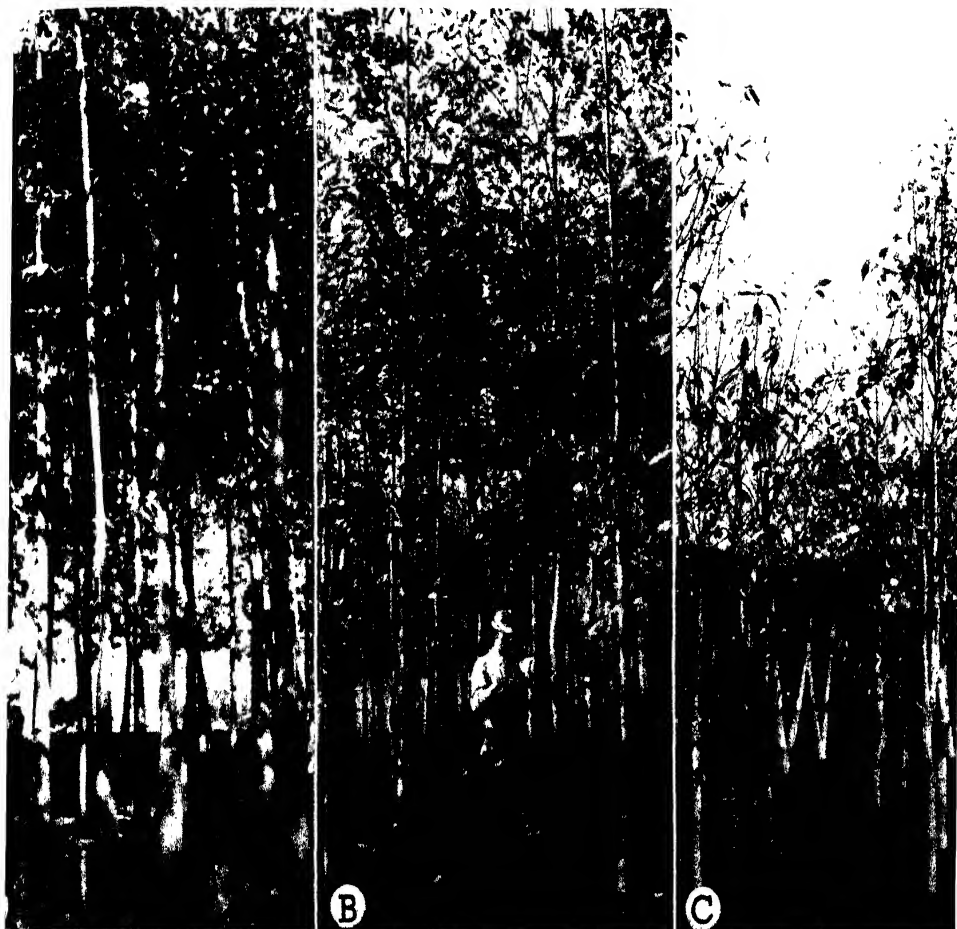


FIG. 3. Twelve-year development of tupelo planted as wildlings on reservoir margins subject to water depth of 1 to 3 feet at normal pool level. (A) Good growth of trees, averaging 3.5 inches in diameter and 29 feet in height, planted on a spacing of 5x5 feet. (B) Crowded trees, averaging only 2.1 inches in diameter and 23 feet in height, planted on the close spacing of 3x4 feet. (C) Poorly-formed trees in 2 feet of water, that have sprouted after die-back caused by water surcharge levels of 5 feet or more covering terminal shoots of trees for prolonged periods during the growing season.

fifteen plantings, eleven and twelve years old, had an average diameter of 3.4 inches. Tally of stems down to a 4-inch peeled top, in 7-foot post lengths, showed a present possible yield of 210 posts per acre from all twelve-year-old plantations and 143 posts per acre from all eleven-year-old plantations. The best planting (Figure 4) showed a present yield of 700 posts per acre. Self-pruning has started on the interior trees. Thinnings can be made in many plantings in the next five years. The cost of thinning may be recovered by utilization of many thinned trees for fence posts.

*Tupelo* (Figure 3), planted at 3 x 4 and 5 x 5 foot spacing, has shown good survival of 88 per cent. The close-spaced stands have developed a very dense canopy and show growth stagnation. These stands average 23 feet in height and 2.1 inches in diameter after twelve years, whereas a stand of the same age planted on a 5 x 5 foot spacing averages 29 feet in height and 3.5 inches in diameter breast high.

*Southern white cedar*, planted as wildlings, has attained exceptionally good height. In one nine-year old planting sample, the dominant trees average 22 feet in height. They have good columnar form (Figure 5) and offer considerable promise for utilization as posts or small poles in view of the wood being inherently durable. The modest survival of 58 per cent is attributed to the poor condition of the wildling stock used to establish this plantation.

#### INJURIOUS AGENTS

Observations on injurious agents affecting the tree plantings studied are included as a note of caution to the worker who might wish to make similar plantings.

In occasional fields where ideal cover had developed following planting, large populations of pine mice were in evidence. Considerable girdling damage was found and in some localities burrows were developed at the base of more than 50 per cent of planted seedlings. Their root systems were gradually being consumed.

Swamp and cottontail rabbits damaged many of the plantations during the first few years by clipping tops out of seedlings. All tree species were susceptible to rabbit damage, but baldcypress, red gum, and green ash were hit heaviest. Most of the clipped seedlings resprouted; the new tops on some were bushy or deformed. These observations suggest that in some localities heavy rabbit populations should be reduced before planting is undertaken.

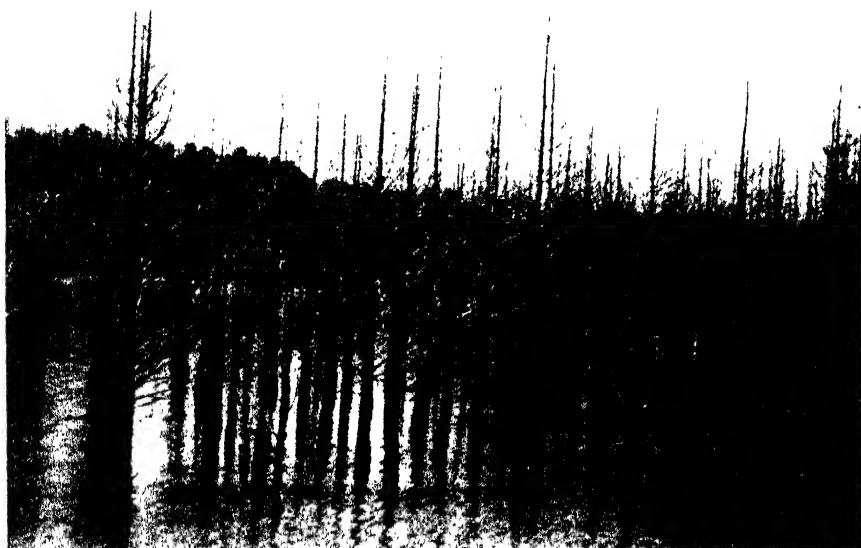
Occasional light infestations of bagworm were noted in some baldcypress plantations. No cases of serious defoliation were in evidence.

A few plantations were damaged by uncontrolled fires and trespass grazing. Such damaged portions were excluded from samples to study plantation response to site. With the exception of southern white cedar and sycamore most of the other trees damaged by fire resprouted. The bushy and deformed tops resulting from fire and grazing damage, however, call for rigid control of these agencies if successful plantation development is to be assured.

#### CONCLUSIONS

Study of 1,100 acres of water-tolerant tree plantations indicates such species as baldcypress, tupelo, southern white cedar, water oak, willow oak, green ash, red gum, and sycamore can be successfully planted along certain margins of artificial reservoirs.

Water-level management is a primary factor controlling the kind of tree to be planted and its location along reservoir margins. Water-tolerant baldcypress, tupelo, and southern white cedar are well adapted to the upper drawdown zone along reservoirs, including flats intermit-



**FIG. 4.** Baldcypress planted eleven years on sites subject to water depth of 1 to 3 feet. (Above) Viewed with water at normal pool level, in March, 1947, this plantation averages 23 feet in height. Established by planting wildlings on a 5x5 foot spacing: Wilson Reservoir, Alabama. (Below) Viewed at time of reservoir drawdown, in October, 1947, with trees still in leaf, this plantation has made excellent development averaging 30 feet in height. Established by planting of 1-0 nursery stock on a 7x7 foot spacing. Pickwick Reservoir, Mississippi.



tently covered with 1 to 3 feet of water. Growth of nine- to twelve-year plantations on first or second class soils unfit for agricultural use, because of water-level management, is as good or better than that of upland plantations of fast-growing pine or hardwoods. Such periodically-flooded sites offer considerable promise for timber production. No information is available to confirm whether any of the other species studied is tolerant of the range of water levels that occur in this zone. Planting below the 3-foot drawdown zone under normal pool level involves considerable risk. Intermittent water levels cover terminal shoots of trees at this elevation long enough during the growing season to result in die-back or death of the trees. Trees that resprout are bushy and deformed.

To date, inherent soil moisture has affected plantation development in the 15-foot surcharge zone above normal reservoir level more than have surcharge levels. Reservoir surcharge that has reached planted trees has occurred chiefly during the dormant season. Surcharge water covering some planting areas 2 to 7 feet throughout most of the dormant season has caused no apparent damage. Only a small portion of the plantings has been flooded for an extended period during the growing season.

Baldcypress, tupelo, and red gum flooded by 2 to 4 feet of "trapped" water from April through June of the third growing season showed no apparent damage. No information is available as to the tolerance of water oak, willow oak, and sycamore to such flooding. However, it is unlikely that the balance of the plantations will ever be subject to extended flooding during the growing season. Trees should continue showing favorable development as long as surcharge levels do not greatly exceed nor extend beyond those occurring during the first five growing seasons. Development of five-year old plantations under these conditions indicate:

1. Tree growth varied by soil series, and best growth was associated with soils having the highest land class and agricultural productivity rating before reservoir impoundment.

2. Soils having compact subsoil are poor planting chances.

3. Plantation growth was found consistent on sites supporting certain ground-vegetation communities. Better growth was made on the lower, moist to wet bottomland soils developing stands of volunteer woody species or rank stands of beggarticks or other hydrophytic weeds; intermediate growth was made on drier sites that developed heavy stands of broomsedge; and poor growth was made where light, scattered broomsedge was admixed with goldenrod, aster and xerophytic weeds.

A summary of the eight water-tolerant tree species planted 5 to 12 years along the margins of fluctuating-level reservoirs on the lower Tennessee River shows the following adaptation to existing soil types and changing water levels:

*Tupelo* is well adapted to flats in the upper drawdown zone that are intermittently covered with 1 to 3 feet of water during the growing



FIG. 5. Southern white cedar in zone covered by 1 to 3 feet of water at normal reservoir pool. Planted wildlings introduced from South Carolina averaged 22 feet in height after nine growing seasons. Judge the height and columnar form by the card at 6 foot height on small cypress in the foreground.

season. In surcharge zones extending 15 feet above normal reservoir level, this tree should be planted only on seepage areas or on sites intermittently flooded during the growing season.

*Baldcypress* is adapted to the same sites as tupelo but can be planted at higher elevations on all but the drier and poorer terrace soils.

*Green ash* is adapted to all sites except those subject to prolonged flooding during the growing season. This tree has been exceeded only by sycamore and willow oak in average total height growth.

*Water* and *willow oak* have not been subject to intermittent flooding during the growing season. They have been found well adapted to all sites in surcharge zones except the drier and poorer terrace soils and those with a compact subsoil. Willow oak has made better height growth than water oak. These two oaks offer promise for cover and food plantings for migratory waterfowl.

*Red gum* is one of the better species for planting on the better terrace soils in the upper part of surcharge zones. This species does well on a great variety of sites and it may prove adapted to moderate and intermittent flooding wherever soils are not compact and slowly drained.

*Sycamore*, represented by only two samples, made better height growth on non-eroded terrace soils in the surcharge zone than any other species studied. The study did not provide information on the tolerance of sycamore to wetter sites or areas subject to moderate and intermittent flooding during the growing season.

Planted wildlings of *southern white cedar* have made excellent growth on areas intermittently covered by 1 to 3 feet of water during the growing season. It has also made good growth in surcharge zones on moist sites most favorable to cypress. Extensive use of southern white cedar in plantings may be limited because nursery stock is not currently available.

Observations on injurious agents affecting the tree plantings showed occasional areas in the surcharge zone heavily infested with pine mice that girdled seedlings or slowly consumed their root systems. Many of the plantations were damaged the first few years by swamp and cottontail rabbits that clipped tops out of seedlings. All species were susceptible, but baldcypress, red gum, and green ash were hit heaviest. Heavy rabbit populations should be reduced in some localities before planting is undertaken. A few plantings were damaged by uncontrolled fires and trespass grazing. Most species resprouted to form bushy, deformed trees. Rigorous protection is essential in order to minimize damage and to assure successful development of reservoir-margin plantations.

#### SUMMARY

A thorough sampling was made of 1,100 acres of water-tolerant tree plantations, five to twelve years of age, along the margins of fluctuating reservoirs on the lower Tennessee River. Data on survival, height, and adaptation of trees to changing water tables and to soil and ground cover conditions were obtained for: baldcypress, *Taxodium distichum*; water oak, *Quercus nigra*; willow oak, *Quercus phellos*; green ash, *Fraxinus pennsylvanica lanceolata*; red gum, *Liquidambar styraciflua*; tupelo,

*Nyssa aquatica*; southern white cedar, *Chamaecyparis thyoides*; and sycamore, *Plantanus occidentalis*. Results were presented for two kinds of reservoir-margin planting sites:

1. Reservoir surcharge zone plantations, ranging from 1 to 15 feet above normal pool level and infrequently flooded during the dormant season have been more affected by inherent soil moisture than by water surcharge levels. Surcharge water covering some areas 2 to 7 feet throughout the dormant season has caused no apparent damage.

Baldcypress, tupelo, and red gum plantations flooded by 2 to 4 feet of "trapped" water through June of the third growing season suffered no apparent damage. No information is available as to the tolerance of water oak, willow oak, and sycamore to such flooding, but it is unlikely the balance of the plantations will be subject to prolonged flooding during the growing season. These plantings averaged from 11 to 90 per cent survival and from 3.5 to 14.3 feet total height growth after five growing seasons.

2. Growth of nine- to twelve-year plantations of baldcypress, tupelo, and southern white cedar in the upper drawdown zone intermittently covered by 1 to 3 feet of water is as good or better than that of upland plantations of fast-growing conifers or hardwoods. Sites made unfit for agricultural use because of water-level management offer considerable promise for timber-production planting.

Planting results in the two zones show: *tupelo* should be planted only on seepage areas or sites intermittently flooded during the growing season; *baldcypress* and *southern white cedar* are adapted to the same sites as *tupelo* but can be planted at higher elevations on all but the drier and poorer terrace soils; *green ash* is adapted to all sites except those subject to prolonged flooding during the growing season; *water* and *willow oak* have not been subject to intermittent flooding during the growing season but offer promise for wildfowl cover and food plantings on all but the drier and poorer terrace soils; *red gum* and *sycamore* are the better species for planting on the better terrace soils in the upper part of surcharge zones.

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# INFLUENCE OF PLANTED TREE BELT IN PLAINFIELD SAND ON EROSION CONTROL AND MOISTURE CONSERVATION<sup>1</sup>

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Extensive areas of sandy outwash plains, produced by water deposition of glacial drift when successive glacial sheets melted in the region of the Great Lakes, have been mapped and classified as the Plainfield group of soils (8). Although inherently low in fertility and water holding capacity, the general topography of these soil areas and the ease with which they could be cleared and tilled, encouraged cropping when settlement took place. They continue in general use for field crop production in Minnesota, Wisconsin, and Michigan.

Plainfield sand and some other sandy soil areas were originally forested with relatively open stands of jack pine (*Pinus banksiana* Lambert), Norway pine (*P. resinosa* Solander), and white pine (*P. strobus* L.) often mixed with northern pin oak (*Quercus ellipsoidalis* E. J. Hill). Inherent danger of wind erosion following land clearing was recognized as early as 1867 (1). The retention of strips or belts of the original tree growth was recommended by King as essential to prevention of soil losses through wind action (2). In practice, however, these recommendations proved of little immediate value due to absence of lower limbs on forest-grown trees, which allowed winds a relatively unhindered sweep. Northern pin oak reproduction developed vigorously in such open belts, and furnished some protection against wind. However, this species proved to be not only relatively short lived, but also an active competitor for moisture and soil fertility with agricultural crops. Ultimately extensive areas of Plainfield soils used for farming became fully exposed to wind.

Wind erosion develops on bare sandy soil when the surface particles become dry and winds, unhindered by natural or artificial obstructions, attain sufficient velocity to cause the rolling and subsequent drifting of sand grains. Its most acute effects are recognized in the removal of clay, silt, and fine sand particles and organic matter from

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<sup>2</sup>The author is indebted to Prof. A. R. Albert, Department of Soils, University of Wisconsin, formerly superintendent of the Hancock Branch Station Farm, for supervision of initial tree planting, the application of the cultural treatments, the data on crop yields and soil temperatures, and for critical reading of the manuscript. Cooperation of the Works Projects Administration is acknowledged for obtaining the measurements of tree heights.

the exposed soil surface, in the undesirable accumulation of drifts, either along fences and highways or as dunes, and in injury of varying degree to all kinds of planted crops. Snow rarely remains on the soil during the entire winter.

#### RELATED STUDIES IN THE EFFECTIVENESS OF TREE BELTS

The influence of shelterbelts on crop yields, shading of soil, moisture sapping, evaporation, movement of soils, and adjacent air temperatures was studied by Bates (3) for central and western areas in the United States. Coniferous and deciduous tree belts were included in this study. Practically all of the tree belts observed were growing on soils heavier in texture than the Plainfield series.

The Purdue Agricultural Experiment Station (4) has records of over 130,000 hours of wind velocity, temperature, and relative humidity to the leeward of five typical Indiana windbreaks. In this study one four-row Norway spruce windbreak 25 feet high, was observed to reduce by 80 per cent the velocity of a 30 miles-per-hour wind at a distance of 50 feet, or twice the height of the trees on the leeward side of the windbreak. The same wind was reduced in velocity 50 per cent at a distance of 150 feet, or six times the height of the trees.

The distance at which the influence of tree belts on winds blowing at right angles to them could no longer be detected or measured has been determined by different workers with widely varying results. Russian workers (5) report that a 50 foot high shelterbelt on the Siberian steppes exerted a measurable influence for two-thirds of a mile to the lee side. The Indiana study (4) showed that for a shelterbelt 25 feet high, measurable influence ceased at between 450 and 500 feet to the leeward.

The influence of tree belts on wind velocity, water retention, accumulation of humus, and agricultural crop yields are summarized by Rudolf and Gevorkiantz (6) in a review of studies made at seven experimental stations in southern Russia and in Siberia. The high silt and clay content of the soils involved in these experimental areas has given results that probably would not be found in distinctly sandy soils, yet it should be noted that quantitative measurements showed wind velocities were reduced at from 210 to 560 feet to leeward of trees 12 to 22 feet high, and planted in belts from 70 to 140 feet wide; increased retention of snow water occurred in the zone of snow drift formation; an increased depth of accumulated humus for distances up to 1,050 feet to leeward of the shelterbelts was noted; and increased yields of rye and wheat grain and straw were obtained within the protected zone on an average of better than three years out of four over a 15 year period.

The function of wind as a factor in soil erosion is the subject of six separate studies by Chepil (7), who states that, "Virtually the whole program of wind erosion control is based on one outstanding consideration, namely, the dependence of all methods of prevention and control on the velocity of wind required to initiate soil movement."

## HANCOCK, WISCONSIN, BRANCH STATION FARM

In May, 1928, the initial planting was made in an eight-row shelterbelt 2,148 feet long, 48 feet wide, and extending in a north-south direction. The objectives of the experiment were four-fold:

1. To secure information on rate of growth and number of years required to produce a relatively effective shelterbelt on Plainfield sand;
2. To observe the comparative value of tree species and mixtures, using (a) all conifers, (b) chiefly deciduous or broadleaf trees, and (c) a combination of both groups;
3. To determine the value of cultivation and applications of commercial fertilizers in promoting the growth of shelterbelts;
4. To determine by quantitative measurements the influence of shelterbelts within measured zones on comparative moisture retention and crop yields.

The area chosen for the experimental shelterbelt was along the west boundary of the farm, and immediately to the east of an unimproved town highway. The soil is very gently undulating Plainfield sand occupying the former bed of glacial Lake Wisconsin. It is low in organic matter and available plant nutrients. It has a reaction varying between pH 5.0 and 5.5. Traces of subsoil development exist at 12 inch to 18 inch depths, but below that the material is medium sand to undetermined depths. The permanent water table, which fluctuates up to 6 feet with periodic precipitation, normally exists at from 10 to 20 feet below the soil surface, depending on surface configuration. Only during short periods of extremely heavy rains or when the soil is frozen, is there any surface water flow.

The date when this land was first cleared of its tree growth, described in 1835 by government surveyors as "scrub oak" and "scrub pine" (jack pine), is not of record. It probably occurred between 1860 and 1870. Neither is there any reliable record of its agricultural use prior to 1916. Between 1916 and 1928 it was used only to produce rye, once in two years, and sometimes only once in three years. In 1928 this land was acquired by the University of Wisconsin, and incorporated into the field pattern of the Hancock Branch Station Farm.

Design of the shelterbelt, choice and arrangement of species, tree spacing, and the plan of cultural treatments were determined after consultation between staff members of the Departments of Agricultural Engineering and of Soils at the University of Wisconsin and of the Lake States Forest Experiment Station, United States Forest Service.<sup>3</sup>

The species of trees selected for the experiment, size and age of stock, and date of initial planting are summarized as follows:

<sup>3</sup> Fred G. Wilson, A. R. Albert, and Carlos G. Bates, respectively.



# LAYOUT DIAGRAM 1

West

Town Road		
Red Cedar Jack Pine White Pine White Pine Norway Pine Norway Pine Norway Spruce White Cedar* Section C—360 Feet 60 Cross Rows All Conifer	Black Locust † Golden Willow American Elm White Pine Norway Pine Silver Maple Green Ash Dwarf Siberian Pea Section B—360 Feet 60 Cross Rows G   F   E   D   C   B   A J   I   H   G   F   E   D   C   B   A Soil Treatments 6 Cross Rows Each	Black Locust † Jack Pine Chinese Elm White Pine Norway Pine Balm of Gilead Jack Pine Dwarf Siberian Pea Section A—1,428 Feet Mixed Planting 22 Cross Rows Not Cultivated 216 Cross Rows Cultivated

Soil Treatments as below, applied annually in April for five years after planting:

A—Not Fertilized—Not Cultivated  
 B—Cultivated and PK  
 C—Cultivated and PK  
 D—Cultivated and LPK  
 E—Cultivated but not fertilized  
 \* Replaced white spruce which failed to survive initial planting.  
 † Removed in 1944.

N = 150 lbs. ammonium sulfate per acre  
 P = 75 lbs. 0-20-0 per acre  
 K = 75 lbs. 0-0-50 per acre  
 L = 150 lbs. ground limestone per acre

<i>Date Planted</i>	<i>Coniferous</i>	<i>Date Planted</i>	<i>Deciduous</i>
1928....	White pine (4 year transplants)	1933.....	Black locust (1 year cutting)
1928..	Norway pine (4 year transplants)	1931.....	Green ash (3 year seedlings)
1928.....	Jack pine (2 year seedlings)	1932..	Balm of Gilead (3 year seedlings)
1932.....	Red cedar (2 year seedlings)	1931.....	Chinese elm (2 year seedlings)
1933..	White cedar (4 year transplants)	1932..	American elm (2 year seedlings)
1930..	White spruce (4 year transplants)	1932....	Silver maple (2 year seedlings)
1929..	Norway spruce (4 year transplants)	1931.....	Golden willow (1 year cutting)
		1931....	Siberian pea (3 year seedlings)

The white cedar replaced a 100 per cent failure of the 1930 planting of white spruce.

Layout, Diagram 1 illustrates the arrangement of species by sections within the shelterbelt, the length of the several sections, and the soil and cultural treatments prescribed for two of the sections.

It will be noted in the diagram showing composition by species that Section A contains hardwoods and conifers in mixture by rows, Section B consists almost exclusively of hardwoods except for the two middle rows, one of white and one of Norway pine, and Section C is comprised entirely of conifers. All trees were planted in check rows at a spacing of 6 by 6 feet.

Annual replacements of losses for all tree species were made through 1936, so that as of January 1, 1937, there were no blanks nor dead trees in the belt. Since it was impossible to determine the cause of losses in all cases, no attempt was made to correlate survival or loss with the several possible factors, principal ones of which were size and condition of stock at time of planting, heat, drouth, and insects.

The period during which the initial plantings were made and the

TABLE 1  
PRECIPITATION AT HANCOCK IN TERMS OF PERCENTAGE OF NORMAL,\*  
1928-40, FOR MONTHS OF MAY, JUNE, JULY, AND AUGUST

Year	Month			
	May (Percentage)	June (Percentage)	July (Percentage)	August (Percentage)
1928.....	50	69	100	145
1929.....	35	89	57	63
1930.....	76	104	126	26
1931.....	12	79	30	90
1932.....	80	97	79	96
1933.....	137	25	108	51
1934.....	31	120	152	78
1935.....	96	114	119	98
1936.....	55	101	32	140
1937.....	88	79	74	92
1938.....	106	134	90	100
1939.....	25	120	49	90
1940.....	89	318	41	310
Normal * .....	4.11 inches	4.47 inches	3.45 inches	3.4 inches

As reported by United States Weather Bureau in its monthly weather reports of 1936.

years immediately following were relatively drouthy and very hot, particularly during the critical months of July and August. Table 1 summarizes the recorded precipitation for the critical months of May, June, July, and August for the years 1928 to 1940 inclusive, in terms of normal precipitation for Waushara County, Wisconsin, as reported in the monthly weather reports issued during the year of 1936 by the United States Weather Bureau.

Several periods of extreme drouth and high midsummer temperatures occurred in June, July, and August before 1934, the critical period in the establishment of trees used in this experiment. The periods of high rainfall for the same months were in 1934 and later. The records of losses sustained in the earlier years of the experiment, and the relatively higher survivals during later years, are comparable to those found for other plantations established between 1928 and 1940 on similar soils.

Extremely high temperatures directly caused some losses in this experimental shelterbelt, especially in July, 1936. In this month there were twelve days with temperature readings above 96° F. On July 12, 13, and 14 of that year the maximum temperature readings were 109°, 111°, and 112°F., respectively. At 12 noon on July 13 a series of temperature readings was made in and adjacent to and directly east of Section C of this shelterbelt, and also southeast of another three-row coniferous snow fence. This proved to be a critical period in the survival of many other young plantations on Plainfield sand in Wisconsin. The following data illustrate the extreme temperatures to which the trees were subjected:

<i>Site of Reading</i>	<i>East of Sec. C.</i>	<i>Southeast of Snow Fence</i>
Air temperature .....	111° F.	108°
Soil surface in the sun .....	144°	153°
1/4" below soil surface .....	147°	170°
3" below soil surface .....	116°	113°
6" below soil surface .....	100°	No reading
Soil surface in shade of planted pine .....	107°	114°

Under these extreme conditions the Norway spruce in this shelterbelt (Section C) suffered a 100 per cent scalding of the 1936 leader growth and of all growth on the sides of the trees exposed to direct sunlight. Approximately half of these Norway spruce later died from the effects of the extreme temperatures; the other half recovered, but were deformed because of loss of leaders and foliage on the south exposures of the trees.

#### GENERAL CULTURAL TREATMENTS

In addition to the special fertilizer treatment described for Section B, all trees were cultivated for several years after planting except the 22

cross rows on the south end of Section A, which remained uncultivated after 1928. All pines in Section A planted in 1928 were cultivated four times during the growing season of that year. No further tillage of any kind was given this section until 1932, when complete cultivation was resumed on all of the section except the south 22 cross rows. The trees were cultivated four times during each of the growing seasons of 1932, 1933, and 1934, and were cultivated once in 1935, after which all cultivation ceased.

#### RESULTS OBTAINED IN THE EXPERIMENTAL BELT

Table 2 shows the mean height and diameter of trees at 4½ feet above the ground for the several species where cultivated (every fifth tree measured), and for all twenty-two trees in each uncultivated row in Section A. The percentage of stand as of December 1, 1939, and the percentage of replacements made from the date of initial planting through 1939 are given also.

Cultivation here produced a growth increase over uncultivated of about 35 per cent for deciduous trees and 8 per cent for the pines. Effect of cultivation on survival was very marked for the Chinese elm and Balm of Gilead, but negligible in the case of conifers, Siberian pea, and locust. Since the primary purpose of cultivating new plantings of conifers is prevention of grass sod formation, it should be stated here that the twenty-two uncultivated cross rows were growing on a slight slope with soil so low in nitrogen that grasses did not form sods thereon for ten years.

Of the pines, jack pine made most rapid early growth, Norway pine next best, and white pine was the slowest in getting started. However, replacements were much greater (about 100 per cent) with white pine and these are, therefore, from one to three years younger.

#### EFFECTS OF FERTILIZER TREATMENTS

Section B of the shelterbelt consists of 60 cross rows (east-west). This section was established to measure, in terms of height growth, the effect of cultivation, and various fertilizer treatments. Table 3 is a summary of height growth recorded at the end of the 1939 growing season.

#### YIELDS OF MIXED ALFALFA, CLOVER, AND TIMOTHY HAY IN RELATION TO DISTANCE FROM SHELTERBELT

In 1939 and 1940 a field of mixed alfalfa, timothy, and red clover, a desirable hay combination on Plainfield sand, lying immediately to the east of the shelterbelt, gave diminishing yields of hay at increasing distances from the shelterbelt. Plots 7 feet wide and 20 feet long were harvested in 1940 to measure this difference. The mean yields of three replicates were as follows:

Distance from Shelterbelt	Lbs. Green Hay per acre	Distance from Shelterbelt	Lbs. Green Hay per acre
10' - 30' .....	6,127	90' - 110' .....	4,672
30' - 50' .....	7,163	110' - 130' .....	4,361
50' - 70' .....	5,919	130' - 150' .....	3,945
70' - 90' .....	4,465		

At the time of this study of hay yields, the belt averaged 17 feet in height. The stand of red clover in the mixture was good within 30 feet of the belt, and became progressively poorer toward the east end of the 165 foot long test plot. With the exception of the nearest plot, the yield of which appears to have been lowered by more intense heat next to the shelterbelt, yields decreased with distance from the belt.

#### LOSSES FROM SNOW, INSECTS, AND DISEASE

In Section C, where white pine is adjacent and to the east, or lee side of jack pine, destruction of white pine leaders and slender upper limbs from the melting and settling of deep snow drifts was much greater than where deciduous trees occurred to the westward. This damage materially interfered with the rate of growth of the white pine in both height and density.

The black locust became infested within two years of planting by the locust borer (*Cyrtene robiniae* Forest) and infestation continued to be so severe that no locust tree reached a diameter of four inches at breast height before it was killed. In 1944 the entire row of locust was pulled out.

Accidentally one Scotch pine was planted in the row of jack pine in Section A. This tree was killed in 1938 by the Scotch pine root collar weevil (*Hylobius radicus* Buchanan). While Scotch pine was not included in the original plan, it was planted later in other shelterbelts on the Branch Station Farm at Hancock, and has been damaged badly by this same insect. The occurrence of the root collar weevil on Scotch pine has resulted in a buildup of the insect population and its subsequent attacks on jack pine with occasional fatal results on this species in the experimental shelterbelt.

No disease has been observed on any of the conifers. The Balm of Gilead has been attacked by a fungus identified as a member of the genus *Nectria* and has been eliminated largely by it. Competition with adjacent Norway and jack pine also contributed to elimination of the Balm of Gilead.

#### CONCLUSIONS

Snow drifts accumulated in the planted tree belt five years after planting, which is evidence that the trees are a factor in reducing wind velocities. At twelve years after planting on Plainfield sand the jack pine in a shelterbelt given five years of cultivation following planting may be expected to reach a height of 17 to 18 feet, Norway pine 15 to

16 feet, and white pine 12 feet. The rate of growth of white pine appears to have been affected adversely because of its position to the leeward side of the rapidly growing jack pine, which caused the formation of heavy snow banks on the flexible white pine and consequent mechanical injury. This caused a material slowing down of the average annual height growth of this species.

The 12-year old experimental shelterbelt exerted a marked favorable influence on the yield of a hay mixture of clover, alfalfa, and timothy for a distance of 70 feet, or approximately four times the height of the tree belt, to leeward, and a measurable influence up to 130 feet, or eight times the height of the belt. More important than this effect appears the immunity that planted crops, and especially legume seedings, would have against being cut down by wind-driven sand particles. The test field, ten rods wide, lying adjacent to and on the lee of this shelterbelt, has been free of damage to crops from westerly winds since 1937 when the largest trees were from 14 to 16 feet in height. On the other hand some damage has been sustained from strong southerly winds, which rarely initiate soil movements.

On the basis of studies reported elsewhere, the width of the zone of favorable influence on crop yields and on soil protection will widen as the trees continue to grow in height. In addition to the volume of snow trapped, and thereby prevented from blowing across the field to leeward, it is apparent that the movement of surface soil is likewise being retarded. A very small accumulation of very fine sand and silt on the leeward side of the belt has been observed.

Greater accumulation of snow occurs within a tree belt eight rows wide than in a three-row belt, and this greater accumulation causes more mechanical damage to the trees. Snow has accumulated up to a depth of ten feet. Snow has been deposited to the leeward side as far as 50 feet beyond the last row of trees. Snow was not blown off the field for even greater distances beyond the shelterbelt.

American elm, golden willow, silver maple, and green ash have made the greatest height growth of the deciduous trees. The relative freedom from mechanical damage in the all-conifer section indicates that no advantage has thus far accrued from planting a mixture of coniferous and deciduous trees in a shelterbelt on Plainfield sand, while conifers sustain some real loss in height growth and vigor.

Black locust proved distinctly objectionable, not only because of the repeated or continuous infestation by the locust borer, but because of many suckers which spread throughout the tree belt and into the roadside and the open field from the parent stock. In the last respect Balm of Gilead proved less objectionable than black locust, but severe damage was caused by cankers, and it, too, spread from suckers. Apparently, it does not compete well on Plainfield sand with jack and Norway pine. Golden willow would apparently make an effective shelterbelt if it were the only tree in the belt, because of its relatively rapid growth and the dense formation of limbs and twigs. Siberian pea

TABLE 2

CULTIVATION EFFECTS ON HEIGHT, DIAMETER, AND STAND OF SEVERAL SPECIES IN SECTION A OF MAIN SHELTERBELT, HANCOCK EXPERIMENT FARM

Row No. From West	Species	Cultivated				Not Cultivated			
		Ht.* (Feet)	Diam.* (Inches)	Replace- ment (%)	Per Cent Stand	Ht.* (Feet)	Diam.* (Inches)	Replace- ment (%)	Per Cent Stand
1	Black locust .....	12.8	1.8	24	95.3	10.9	1.7	9	100.0
3	Chinese Elm .....	10.5	1.4	84	87.5	5.2	0.9	107	63.6
6	Balm of Gilead .....	9.3	0.7	3	68.6	7.8	1.0	7	9.1
8	Caragana .....	4.9	†	17	99.1	3.9	†	15	100.0
	Mean .....	9.35	1.3	..	..	6.95	1.20	..	..
2	Jack pine .....	15.6	3.2	49	100.0	14.2	3.6	57	100.0
4	White pine .....	7.8	0.9	72	92.6	6.4	0.8	75	100.0
5	Norway pine .....	12.4	2.7	21	99.5	11.9	2.2	18	100.0
7	Jack pine ....	15.5	3.4	47	100.0	15.1	3.3	47	100.0
	Mean .....	12.82	2.25	..	..	11.9	2.47	..	..

\* Mean height and diameter is for surviving trees, Oct. 1, 1939.

† Not measurable.

TABLE 3  
MEAN TREE HEIGHTS ATTAINED BY OCTOBER 1, 1939, IN SECTION B, FERTILIZER SERIES

Treatment	Mean Height*							
	Row 1 Black Locust	Row 2 Russian Willow	Row 3 American Elm	Row 4 White Pine	Row 5 Norway Pine	Row 6 Silver Maple	Row 7 Green Ash	Row 8 Caragana
A No cultivation, no fertilization .....	(feet)	(feet)	(feet)	(feet)	(feet)	(feet)	(feet)	(feet)
B Cultivated. P-K .....	11.0	8.4	3.7	8.6	12.7	2.4	3.8	4.8
C Cultivated. K .....	12.4	12.4	4.6	6.9	13.3	6.8	6.2	5.7
D Cultivated. P-K-L .....	15.1	16.0	5.7	10.9	14.2	8.5	6.0	5.3
E Cultivated, no fertilization .....	14.6	9.2	7.2	11.4	14.3	7.1	9.4	5.7
F Cultivated. N-P-K .....	12.6	8.5	5.3	10.4	13.6	8.5	9.8	4.4
G Cultivated. 2N-P-K .....	14.0	13.3	7.1	11.9	13.5	10.8	9.2	5.5
H Cultivated. N-P-2K .....	12.4	10.4	7.0	8.6	14.0	9.3	9.0	5.9
I Cultivated. P-K. Legumes interplanted.	15.3	8.2	4.7	8.7	13.9	10.3	10.2	4.6
J Cultivated. N .....	16.4	7.1	6.5	10.3	14.2	8.5	9.6	5.5
	12.6	13.8	7.7	9.6	12.9	6.2	8.6	4.3

\* Mean height is average height of actual number of surviving trees.



and red cedar have not attained much height but have maintained a dense leaf and twig barrier. Their greatest usefulness in a shelterbelt is maintaining a barrier close to the ground when the lower limbs of the conifers die off from shading. Obviously, they should occupy outside rows. Although Siberian pea has formed seed profusely, none of the seeds have produced volunteer seedlings thus far.

Cultivation in the early growth of all species showed marked, favorable influence, but was most pronounced on green ash, American elm, white pine and silver maple. None of the conifers were benefited appreciably by nitrogen, but deciduous trees were favorably affected. White pine gave erratic results and meager response to fertilizer treatments. Norway pine gave extremely slight but consistent response to all types of fertilizer applications.

The important legume hays, red clover and alfalfa, in mixture with grass hay, normally difficult to hold in long rotations on Plainfield sand, survived well in the zone of influence of the shelterbelt. There are two possible explanations for the higher yields of hay occurring near the shelterbelt. The first is that the melting of accumulated snow in the leeward drift and under the trees increased the soil moisture supply. Yet it is known that sands are notably weak in their ability to retain water. The second and more probable explanation is that the accumulated snow did not melt completely until after the occurrence of the most damaging periods of alternate freezing and thawing weather. Thus the underlying clover and alfalfa suffered decreasingly less winter injury in the direction of approach to the shelterbelt.

#### SUMMARY

1. An experimental eight-row shelterbelt, composed of conifers and hardwoods, was established between 1928 and 1932 on a field of Plainfield sand on the Hancock Branch Station Farm, University of Wisconsin, College of Agriculture, to determine the rate of growth of trees and the length of time necessary to obtain an effective shelterbelt on this soil type, to compare the relative effectiveness of conifers in mixture with deciduous trees and conifers alone, to determine the value of cultivation and the use of fertilizers in stimulating rate of growth, and to measure the influence on crop yields of a shelterbelt growing on Plainfield sand.

2. Above-average temperatures and drouth periods during growing seasons the first five years after planting caused high mortality in the initial tree plantings after 1928.

3. Coniferous trees averaged 17 feet in height at 10 years of age, and at this height were effective in trapping snow on the adjacent field to the leeward side and in protecting soil and crops against west wind injury.

4. Cultivation for the first five years after planting stimulated tree height growth moderately. The application of nitrogen benefited

deciduous trees somewhat, but did not increase the growth rate of conifers. The application of potassium alone, and potassium with phosphorus gave only slightly more favorable growth rates than no treatment.

5. None of the deciduous species used showed general thrift and dense foliage on this Plainfield sand. Black locust suffered extremely severe damage from the locust borer, produced vigorous suckering, and at the end of 15 years was removed, to prevent damage to other trees in the belt.

6. Legume hays in mixture with grasses, principally timothy, continued thrifty where they had the benefit of a continuous blanket of snow deposited on the leeward side of the shelterbelt.

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## AUTHOR INDEX

- Bartholomew, William Victor, 3  
Becker, Elery R., 239  
Broadbent, H. Smith, 5  
Brouns, Richard J., 129, 150  
Brush, Miriam, 8  
Bryant, Jay C., 269
- Carlander, Kenneth D., 185, 227  
Chao, Tsai S., 126  
Chapman, A. G., 323  
Chase, Clarence D., 333  
Christian, Robert V., Jr., 11  
Clark, Russell N., 15  
Curtis, Ross, 91
- Davis, E. M., 341  
Diehl, Harvey, 91, 110, 126, 129, 141, 150,  
165  
Dube, Harvey Albert, 19  
Duerr, William A., 349  
Dunn, Paul M., 363
- Fassel, Velmer Arthur, 21  
Feng, Chao Lin, 24  
Fullhart, Lawrence, Jr., 27
- Gainer, Gordon C., 29  
Getty, Russell E., 319  
Gibbs, J. A., 371  
Graham, Lewis Texada, 33
- Hach, Clifford C., 91, 110, 150, 165  
Harrison, George C., 91, 110, 129, 150  
Hartman, George B., 319  
Henselmeier, Lois, 110  
Hicks, Ellis A., 36  
Hill, Roscoe Earle, 39  
Hurd, Richard M., 387
- Isely, Duane, 197
- Jenkins, Merle T., 205  
Johnson, Helen Virginia, 42
- Kansky, George W., 395  
Klemme, Randall T., 44  
Knippling, Edward, 47
- Larsen, J. A., 319, 405  
Levine, Melvin Lewis, 53  
Lewis, William M., 185  
Liggett, Lawrence M., 91, 110, 129, 141,  
150  
Lysenko, Michael G., 239
- MacAlpine, David Muir, 50  
McLintock, Thomas F., 415  
McNew, George L., 177  
Magee, Jean Anne, 257  
Mathews, John, Jr., 110  
Mero, Lorraine Anne, 55  
Mikus, Felix F., 58  
Minges, Philip A., 61
- Parmelee, Carlton Edwin, 64  
Peters, Isaac I., 66
- Reese, Hamit Darwin, 68
- Scholz, Harold F., 421  
Schwandt, R. W., 110  
Sigler, William Franklin, 71  
Silker, T. H., 431  
Slater, C. S., 269  
Slosberg, Harry Marshall, 74  
Speeter, Merrill E., 76  
Sprague, G. F., 205  
Stevens, Frank J., 79  
Stone, William Matthewson, 81, 215
- Thornton, George Daniel, 84  
Trenk, Fred B., 449
- Ward, Mary Jane, 87  
Watts, Lyle F., 317



## SUBJECT INDEX

- Albumen, liquid egg, factors affecting functional properties of, 74
- Alkyl halides, amylose complexes with, 58
- Amylolytic agents, employed in alcoholic fermentation, 68
- Amylolytic enzymes, linear and cyclic amylo-oligosaccharides relationship to, 53
- Amylo-oligosaccharides, linear and cyclic, relationship to amylolytic enzymes, 53
- Amylose complexes, with organic acids and alkyl halides, 58
- Animal organism, utilization of nitrogen by, 8
- Antibodies, the production of, 87
- Arch-ribs, cracking of thin concrete walls poured with, 50
- Belinda silt loam soil, effect of crop rotation on soil aggregation in, 24
- Biology, of tuber flea beetle, 39
- Calcium arsenate, field investigation of, 33
- Cheese, blue, manufacture from pasteurized milk of, 64
- Chemotherapeutic agents
  - nitrogen and sulfur compounds, 5
  - insecticides and drugs as, 47
- Chi-square, abridged form, field investigation of, 33
- Cobalt compounds, oxygen-carrying, studies on:
- VIII. Analogues of disalicylalethylene-diimine cobalt with *o*-hydroxycarbonyl compounds other than salicylaldehyde, 91
- IX. Analogues of disalicylalethylene-diimine cobalt with diamines other than ethylenediamine, 110
- X. Cobalt derivatives of the Schiff's bases of salicylaldehyde with alkylamines, 126
- XI. Oxygen-carrying compounds derived from mixtures of *o*-hydroxyaldehydes, 129
- XII. Attempted synthesis of an unsymmetric Schiff's base of ethylenediamine, 141
- XIII. Apparatus for determining the capacity and rate of oxygenation of solid materials, 150
- XIV. Design of apparatus for the manufacture of oxygen using co-ox and its derivatives, 165
- Codling moth sprays, spreading agent for, 33
- Conservation, forest, low-income landholding a problem in, 349
- Corn seed, treated, effect on growth of swine of, 177
- Crop rotation, effect on soil aggregation of, 24
- Decomposition, biological, of plant materials, 3
- Diameter-growth, studies of northern red oak, 421
- Drugs, as chemotherapeutic agents, 47
- Duff moisture, relation to forest fires of, 405
- Ecology, factors affecting the activity of western fox squirrel, 36
- Enzymes, amolytes, 53
- Epitrix tuberis* Gentner, 39
- Erosion control
  - growth of tree plantings for, 371
  - influence of tree belt on, 449
- Fermentation, alcoholic, amylolytic agents employed in, 68
- Finite differences, application of generalized Laplace transformation to problems involving, 81
- Forest fires, relations with unusual weather conditions, humidity, duff moisture, and inflammability, 405
- Forest products, research in Oregon, 363
- Frozen storage, water content changes of poultry in, 42
- Functional groups, introduction into organosilanes of, 15
- Gamma-valerolactone, some derivatives of, 11
- Helides, alkyl, 58
- Histology, structure of the stem of *Zea mays* in relation to stiffness of stalk, 257
- Humidity, relation to forest fires of, 405
- 3-Indoleacetic acids, 79
- Inflammability, relation to forest fires of, 405
- Insecticides, as chemotherapeutic agents, 47
- Iodine, reaction with starch and the Schardinger dextrans of, 19
- Isoquinoline, mechanisms of addition of organolithium compounds to, 29
- Landholding, low-income, a problem in forest conservation, 349
- Laplace transformation, generalized, 81
- Laplace transforms, generalized, a list of, 215

- Lead arsenate, field investigation of, 33
- Legumes, effect of nitrogen fertilization on, 84
- Lepibema chrysops* (Rafinesque), 71
- Lipolytic enzyme system, of *Mycotorula lipolytica*, 66
- Logs, "woods waste," lumber recovery from, 341
- MacDonald, G. B., 319
- Metabolism, of tyrosine isomers and analogues, 76
- Methionine, as main source of nitrogen in the diet of the rat, 8
- Milk, pasteurized, manufacture of blue cheese from, 64
- Moisture conservation, influence of tree belt on, 449
- Moisture content, influence on biological decomposition, 3
- Morone interrupta* Gill, 185
- Mycotorula lipolytica*, lipolytic enzyme system of, 66
- Nebraska, biology and control of the tuber flea beetle in, 39
- Nitrogen  
  animal organism utilization of, 8  
  factor in sweet potato production, 61
- Nitrogen compounds, as chemotherapeutic agents, 5
- Nitrogen fertilization, effect on legumes of, 84
- Nitrogen nutrition, of legumes, effect of nitrogen fertilization on, 84
- Northeast, evaluation of tree risk in the spruce-fir region of, 415
- Noxious weed, examinations, time saving methods, 197
- Nylon, the mordanting with potassium dichromate of, 55
- Oak, northern red, diameter-growth studies of, 421
- Oregon, forest products research in, 363
- Organic acids, amylose complexes with, 58
- Organolithium compounds, mechanisms of addition to quinoline and isoquinoline of, 29
- Organosilanes, introduction of functional groups into, 15
- Palatability, relation of water content changes of poultry to, 42
- Parasites, blood sucking, external, chemotherapeutic agents for, 47
- Pine, shortleaf, survival and growth of various grades of, 323
- Plainfield sand, influence of planted tree belt on erosion control and moisture conservation in, 449
- Plant materials, biological decomposition of, 3
- Potassium dichromate, the mordanting of cellulose-acetate rayon, nylon, and silk with, 55
- Poultry, frozen storage, water content changes of, 42
- Quinoline, mechanisms of addition of organolithium compounds to, 29
- Range condition, judging in range inventory project of, 395
- Range inventory project, judging range condition and trend in, 395
- Range trend, judging in range inventory project of, 395
- Rare earth elements, quantitative spectrographic analysis of, 21
- Rats, reinfection with *Trypanosoma lewisi* of, and recurrence of reproduction in, 239
- Rayon, cellulose-acetate, the mordanting with potassium dichromate of, 55
- Reproduction, recurrence in recovered and near-recovered rats of, 239
- Reservoirs, fluctuating-level, planting of water-tolerant trees along margin of, 431
- Rigid frames, cracking of thin concrete walls poured with, 50
- Runoff water, agent in loss of soluble materials from soils, 269
- Schardinger dextrans, reaction of iodine with, 19
- Sciurus niger rufiventer*, 36
- Silk, the mordanting with potassium dichromate of, 55
- Silviculture, implications of diameter-growth studies of northern red oak, 421
- Soil aggregation, effect of crop rotation on, 24
- Soils, loss of soluble materials from, 269
- Soluble materials, runoff water as agent in loss of, 269
- Southeastern region, growth of tree plantings for erosion control in, 371
- Species adaptability, range test of, 387
- Spectrographic analysis, quantitative, of rare earth elements, 21
- Spruce-fir region, evaluation of tree risk in, 415
- Starch, reaction of iodine with, 19
- Stizostedion vitreum vitreum* (Mitchill), 227
- Sulfides, alkylamino, 27
- Sulfones, alkylamino, 27
- Sulfur compounds, as chemotherapeutic agents, 5
- Sweet potato, nitrogen factor in production of, 61
- Swine, effect of treated corn seed on growth of, 177

- Tallying, cumulative, 333  
Tax, graduated land, 44  
Temperature, influence on biological decomposition, 3  
Tetrachloro-parabenzquinone, effect on growth of swine, 177  
Tree belt, influence on erosion control and moisture conservation of, 449  
Tree plantings, for erosion control, growth of, 371  
Tree risk, evaluation in spruce-fir region of, 415  
Trees, water-tolerant, planting along fluctuating-level reservoirs of, 431  
*Trypanosoma lewisi*, reinfection of rats with, 239  
Tuber flea beetle, biology and control of, 39  
Tyrosine, isomers and analogues of, 76  
Walls, thin concrete, cause and prevention of cracking in, 50  
Water content, changes in poultry in frozen storage of, 42  
Waxy corn, development for industrial use of, 205  
Weather conditions, unusual, relation to forest fires of, 405  
Western fox squirrel, the activity of, 36  
White bass, life history and management of, 71  
Yellow bass, growth of, 185  
Yellow pikeperch, growth of, 227  
*Zea mays*, histological structure of the stem of, 257





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